

Light Emitting Diodes (LEDs)

Light emitting diodes (LEDs) are one of the main sources of gallium being investigated in the ReGaLL project. It is thus appropriate to give an introductory overview of these innovative energy-efficient devices that are changing the way we approach lighting. Although LEDs have only recently become predominant in a wide range of lighting applications, they have actually been around for many decades. The initial discovery of light emission from a solid-state diode was made over 100 years ago, while the first infra-red emitting devices were produced in the 1950s. During the 1960s, there was a lot of R&D work to move the wavelength of the light emitted into the visible part of the spectrum and to improve output efficiencies so that they could be used commercially. The initial material used to make LEDs was gallium arsenide and new materials were needed that could be made to emit light at ever shorter wavelengths. The first visible LEDs were red and then came orange, yellow and green emitters. One popular material for these devices was gallium phosphide, with related compounds being gallium arsenide phosphide, aluminium gallium phosphide, gallium nitride and indium gallium nitride. Examples of typical LED materials and their emission wavelengths are shown below.

Material	Wavelength/nm	Colour
Aluminium nitride (AlN) Aluminium gallium nitride (AlGaN) Aluminium gallium indium nitride (AlGaInN)	400	Ultraviolet
Indium gallium nitride (InGaN)	400-450	Violet
Indium gallium nitride (InGaN) Silicon carbide (SiC)	450-500	Blue
Gallium phosphide (GaP) Aluminium gallium indium phosphide (AlGaInP) Aluminium gallium phosphide (AlGaP)	500-570	Green
Gallium arsenide phosphide (GaAsP) Aluminium gallium indium phosphide (AlGaInP) Gallium phosphide (GaP)	570-590	Yellow
Gallium arsenide phosphide (GaAsP) Aluminium gallium indium phosphide (AlGaInP) Gallium phosphide (GaP)	590-610	Orange
Aluminium gallium arsenide (AlGaAs) Gallium arsenide phosphide (GaAsP) Aluminium gallium indium phosphide (AlGaInP) Gallium phosphide (GaP)	610-760	Red
Gallium arsenide (GaAs) Aluminium gallium arsenide (AlGaAs)	>760	Infrared

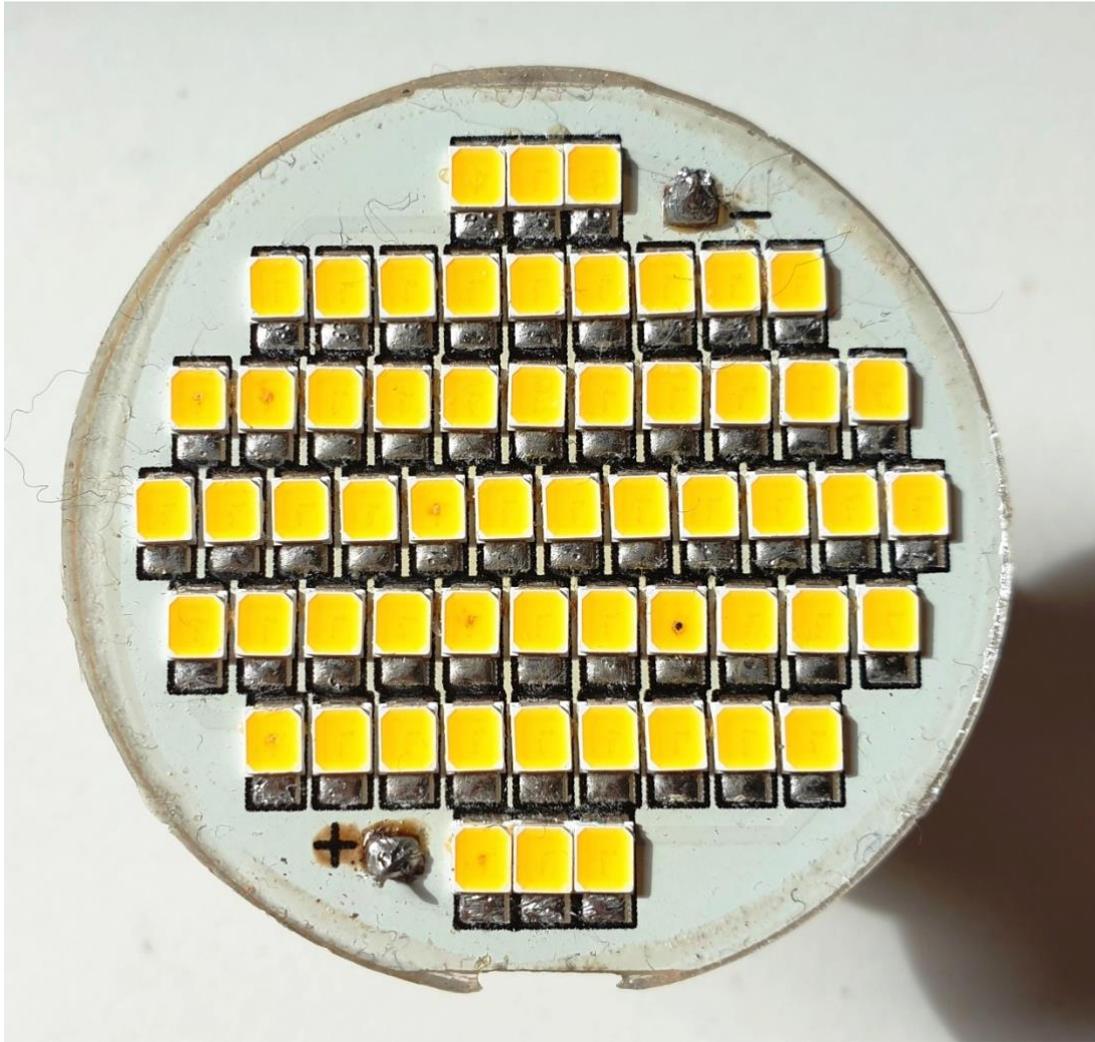
It is interesting to note that, since their invention, a very high proportion of LEDs have contained gallium, the metal of interest for the ReGaLL project.

Unlike incandescent lamps, which emit light by passing a current through a wire filament, LEDs are pure solid-state devices and light is generated when electrons pass between two different types of the same material. For example, a LED made of gallium phosphide (GaP) will have two different types of GaP. One side will be P-type and the other will be N-type. These differences are produced by a doping process that introduces impurities into the crystal structure. This effectively means that there are either additional free electrons, or holes where electrons can be accommodated. If the material has free electrons, it is known as N-type and with extra holes it is known as P-type. A diode has N and P type material regions next to each other and they form what is known as a depletion layer at the P-N junction. When such a diode is appropriately biased, electrons can move from the N-type to the P-type material, where they can enter holes. During this process, the electrons lose a specific amount of energy and it is emitted in the form of photons that are responsible for producing the light emissions. The amount of energy emitted is specific to the material and the colour of the light (corresponding to the energy of the photons) is determined by the difference in discrete energy levels (or band gap) found in the material that has been used to make the LED.

For many years, LEDs were limited to single colours and they were initially used as equipment indicator lamps, or in simple seven segment displays found in early calculators. Sometimes, different coloured LEDs were placed in the same package, e.g., red and green, but these were still fairly limited. The big opportunity was for LEDs to be used in lighting and display applications but there were two problems. Firstly, white light is needed for illumination and, secondly, LED light outputs were very low and unable to compete with traditional incandescent sources. In order to make a white light LED, it is necessary to combine various colours of the visible spectrum, and this includes a shorter wavelength blue colour. Without a blue LED it was not possible to mix three colours to produce the white light. Unfortunately, for many years, and despite a lot of research, it was thought that it would not be possible to produce a blue LED because there were no known materials with the requisite wide enough band gap. Eventually, magnesium-doped gallium nitride was identified as material that could be made to emit blue light, but it was difficult to manufacture, and the light output was low. Fortunately, there has been a huge amount of work on GaN with many improvements being made in the manufacturing processes and in achieving much higher outputs. For example, gallium nitride is now grown as a thin film on an alternative substrate material such as silicon. This enables well-established semiconductor processing techniques to be used, while also reducing the cost and avoiding the difficulties encountered when growing the bulk material. A selection of discrete LED devices is shown below.



Once blue LEDs with good performance became available, it was possible to make devices that appeared to emit white light. This was initially achieved by using a combination of red, green and blue LEDs. However, the actual nature of the white light produced using this approach was not truly white and did not meet the requirements for many lighting applications. Consequently, a different approach has now been more widely adopted and it uses a combination of a blue LED and phosphorescent materials. Essentially, some of the blue LED light is used to stimulate specially developed phosphors that then emit other colours in the visible spectrum i.e., red, green, yellow and orange. By carefully selecting the phosphors, different colour outputs can be achieved and thus the specific nature of the white light determined, e.g., cool or warm white. An array of LEDs taken from a 5-Watt GU10 lamp is shown below.



In terms of gallium and its recovery, it is clear that the world will continue to transition away from incandescent lighting to the use of LEDs. As their performance improves further and costs reduce, more and more applications will use LEDs to provide lighting. This growing volume of LEDs will also lead to greater numbers of devices reaching end of life and thus the opportunity for gallium recovery and reuse will also increase. It will also mean that projects like ReGaIL, which aim to develop new gallium recycling technologies, will become more important if we are to use truly sustainable and circular economy approaches with this valuable critical raw material.

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