Determination of Chromaticity Coordinates and Bandgaps of III-V LEDs Using Electroluminescence Spectroscopy

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Introduction

In 1907 English engineer Henry Joseph Round was testing the rectifying current behaviour of SiC crystallites and noticed that a faint yellow light was emitted from the SiC; this was simultaneously the first reported observation of the phenomena of electroluminescence and the first successful operation of a light emitting diode (LED).^{1,2} The work of Round was expanded on by a few others in the early 20th century,^{2,3} but it would take many decades for LEDs to become efficient enough for practical use.² In the 1960s the first commercial LEDs were released which had emission in the NIR and red regions of the spectrum. It would take another 30 years for the breakthrough of high efficiency InGaN based blue and green LEDs, in the late 1990s, to usher in the age of the LED.

Modern LEDs are efficient, bright and reliable and are one of the most versatile and widely used light sources with an ever increasing number of applications. LED technology is still advancing at a rapid pace with new device architectures and doping methods being developed in order to increase LED brightness and efficiencies. In addition there are several new disruptive LED technologies using quantum dots (QDLEDs), organic semiconductors (OLEDs) and halide perovskites (PLEDs) which are set to move LED design away from the classic type III-V semiconductors that have previously dominated the technology. An essential technique to characterise new LED designs and advance their development is electroluminescence (EL) spectroscopy. In EL spectroscopy a current is passed through a light emitting device and the properties of the emitted light studied; in either a steady state or time-resolved measurement. In steady state EL spectroscopy a constant current is passed through the device and the EL emission spectrum measured using a monochromator. From the emission spectrum the chromaticity coordinates and colour rendering index of the emission can be calculated, in addition to fundamental material properties such as the bandgap of the semiconductor. In time-resolved EL spectroscopy the EL response of the device to short voltage pulses is studied in order to investigate the dynamics of charge carriers in the device, such as triplet formation in OLEDs.



Figure 1 FS5 Spectrofluorometer which can be equipped with a range of source measure units and function generators for the measurement of steady state and time-resolved electroluminescence.

In this application note the FS5 Spectrofluorometer equipped with the electroluminescence accessory is used to investigate the emission properties of four type III-V LEDs and determine their bandgaps and chromaticity coordinates.

An LED is composed of layers of semiconducting material that are doped to be either p-type or n-type. A p-type semiconductor is one that contains an excess of holes while an n-type has an excess of electrons. The first commercial LEDs used a simple p-n junction structure where a p-type and n-type region were brought together and electrons and holes recombined at the interface to generate light. However this simple structure is not very efficient and modern LEDs use what is known as a double heterojunction structure to maximise LED efficiency. A schematic of a double heterojunction structure is shown in Figure 2 and consists of two p-n junctions at the interfaces between three different semiconductor regions. When a voltage is applied across the semiconductor the holes in the p-type region and electrons in the n-type region will drift towards the p-n junctions and enter the active region. Since the active region has a lower bandgap than the flanking n-type and p-type regions, the electrons and holes become energetically trapped in this region and are therefore more likely to recombine. The recombination of the electrons and holes generates light with an energy equal to the bandgap (E_{o}) of the active region.



p-type semiconductor active semiconductor n-type semiconductor

Figure 2: Double heterojunction light emitting diode band structure. Holes are shown as hollow circles and electrons as filled circles. Recombination of electrons and holes generates photons with an energy equal to E_g (active). Adapted from Wagner.⁴

The vast majority of conventional LEDs are constructed of III-V compound semiconductors. A III-V semiconductor is an alloy containing elements from groups III (B, AI, Ga, In) and V (N, P, As, Sb) of the periodic table. For blue and green LEDs the elements used are In, Ga and N. The p-type and n-type regions in these LEDs are formed from GaN which has a large bandgap of 3.4 V (360 nm), and the ratio of Ga to N is adjusted to make it p-type or n-type. The active region of the LED is formed from In_xGa_{1.x}N, where the inclusion of indium lowers the bandgap of the semiconductor. By changing the ratio of In to Ga, the bandgap and therefore the emission wavelength and colour of the LED can be tuned.

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As the In content is increased, InGaN LEDs become increasingly inefficient and it is therefore not practical to make LEDs with peak emission wavelengths greater than ~550 nm using InGaN. The most popular semiconductor to cover wavelengths beyond ~550 nm is $(Al_xGa_{1.x})_{0.5}In_{0.5}P$. By increasing the ratio of Al to Ga (higher x) the bandgap is increased and the emission wavelength of the LED is blue shifted. Using electroluminescence spectroscopy the peak emission wavelength of InGaN and AlGaInP LEDs can be measured and the bandgap energy of the active region and elemental composition of the LEDs determined.

Materials & Methods

Commercial light emitting diodes were purchased from Farnell Ltd; blue (OVL-5523), green (OVL-5524), orange (OVL-5528), and red (OVL-5526). Electroluminescence spectra were measured using the FS5 Spectrofluorometer equipped with a PMT-900 detector. A source measure unit was used to apply a voltage across the LEDs, with the voltage adjusted until the current through the LED was 20 mA.

Results & Discussion

The emission spectra of four III-V LEDs were measured using the FS5 and are shown in Figure 3. The blue and green LEDs are based on InGaN and have peak emission wavelengths of 462 nm and 516 nm respectively while the yellow and red are based on AlGaInP with wavelengths of 594 nm and 630 nm.

For display applications it is more common to classify the emission of an LED by its chromaticity coordinates rather than the peak wavelength. The Fluoracle® software of the FS5 has a built-in wizard to generate a chromaticity plot from any emission spectrum, in either CIE 1931 or CIE 1976 colour space. The chromaticity coordinates of the four LEDs were calculated in CIE 1931 colour space and are shown in Figure 4.



Figure 4: Chromaticity coordinates of the emission from the four LEDs in CIE 1931 colour space, calculated using Fluoracle from the electroluminescence spectra in Figure 3.

Using the information gained from the electroluminescence spectra, the bandgap of the active region of each LED can be simply determined by converting the peak wavelength of the LED emission into energy units (Table 1). The bandgap energy can then be used to determine the composition of the semiconductor in the active region of the LED.



Figure 3: Electroluminescence spectra of InGaN and AlGaInP LEDs showing the peak wavelengths and FWHM of the emission. The voltage applied to each LED was adjusted to achieve a current of 20 mA. $\Delta \lambda_{em} = 0.1$ nm.

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For InGaN LEDs an empirical relationship between the bandgap energy and the composition has previously been established to be, 2

$$E_{g} = E_{g}^{GaN} + (E_{g}^{InN} - E_{g}^{GaN}) x - x (1-x) E_{b}$$
 (1)

where E_g is the bandgap of $In_xGa_{1-x}N$, E_g^{-GaN} and E_g^{-InN} are the bandgaps of GaN and InN which are 3.42 eV and 0.77 eV respectively,² x is the ratio of In to Ga and E_b is the bowing parameter which has been empirically found to be 2.4 eV.^{2,5} Inserting these values and the bandgaps from Table 1 into Eq. 1 and solving the quadratic equation, gives x values of 0.16 and 0.23 for the blue and green LED respectively.

For AlGaInP the following relationship between the bandgap and the composition of the semiconductor has been found, $^{\rm 2}$

$$E_{g} = E_{g}^{GalnP} + 0.61x$$
 (2)

where E_g is the bandgap of $(Al_xGa_{1,x})_{0.5}In_{0.5}P$, E_g^{-GalnP} is the bandgap of $Ga_{0.5}In_{0.5}P$ and x is the ratio of Al to Ga. Inserting the literature value of E_g^{-GalnP} of 1.91 eV,² and the bandgaps from Table 1 into Eq. 2 gives x values of 0.30 and 0.10 for the yellow and the red LEDs respectively.

Table 1: Peak wavelengths, bandgaps and elemental composition of four III-V LEDs

Colour	Peak Wavelength (nm)	Bandgap (eV)	Composition
Blue	462	2.68	In _{0.16} Ga _{0.84} N
Green	516	2.40	In _{0.23} Ga _{0.77} N
Yellow	594	2.09	(Al _{0.30} Ga _{0.70}) _{0.5} In _{0.5} P
Red	630	1.97	(Al _{0.10} Ga _{0.90}) _{0.5} In _{0.5} P

Conclusion

The emission properties of four III-V LEDs were measured using the FS5 Spectrofluorometer equipped with the electroluminescence accessory. From the electroluminescence spectra the peak wavelengths, FWHM and chromaticity coordinates of the LED emission were calculated. From the peak emission wavelengths the bandgaps and elemental composition of the semiconductors were determined, demonstrating the utility of electroluminescence spectroscopy. The capability of both the FLS1000 and FS5 spectrometers can be extended with a range of electroluminescence accessories for the characterisation of electrical devices.

References

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For more information, please contact:

Edinburgh Instruments 2 Bain Square, Kirkton Campus Livingston United Kingdom EH54 7DQ

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