



*This is a preview version of our white paper on LED and photodiode photonic devices*

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WHITE PAPER

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## Broadband radiometric measurement of light-emitting diodes with a photodiode

The spectral characteristics of the light-emitting diode (LED) and the photodiode are well explained by quantum mechanics. Based on this knowledge, we will demonstrate how our multi-wavelength LED light source can be measured with a photodiode.

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The spectral power distribution of a light-emitting diode (LED) has a distinctive asymmetrical gaussian shape. This is the macroscopic expression of finely tuned properties buried inside the semiconductor. In this white paper, we unveil why and how a photodiode can be used as a reliable radiometric instrument for the characterisation of broadband LEDs. The key idea is to use prior knowledge of the centroid wavelength  $\lambda_c$  of the emitted light and account for it to calculate the responsivity  $\mathfrak{R}(\lambda_c)$  of the photodiode.

## 1. Introduction

Basic science is primarily a discipline based on observation. Many fundamental discoveries owe much to the quality of the underlying observations, *i.e.* the precise and accurate measurement of phenomena. A fascinating story that illustrates this is that of Kepler's laws describing the motion of the planets around the Sun. If Johannes Kepler succeeded to make his extraordinary discoveries, it is undeniably because he had extremely accurate data from Tycho Brahe, especially his meticulous observations of Mars recorded over a whole decade. Kepler, who had been Brahe's assistant, knew that these data were absolutely reliable, and definitely the most accurate at the time.

The discovery of quantum mechanics is also closely linked to the development of accurate instrumentation, particularly that used for the build and characterisation of blackbody radiation. Here, we are interested in the spectral characterisation of LEDs. In section 3, we will present the study of blackbody radiation and see that it is a very suitable entry point to tackle this subject. Our approach being made from a historical perspective, this will lead us to talk about the discovery of the photoconductive effect in section 4. Section 5 will be devoted to semiconductor properties and their use in photonic devices: the photodiode, whose responsivity model will be presented in section 6; the LED, whose characteristic electroluminescence spectrum will be explained in section 7. Finally, in section 8, with the help of the technical developments presented in previous sections, we will be able to develop the main idea of this document: namely, the use of the photodiode for radiometric measurement of broadband LEDs. Before that, we will first introduce in section 2 the fundamental constants that will be used throughout this paper.

## 2. The seven defining constants of the International System of units

As early as 1900, Max Planck suggested that the two constants  $k_B$  (now known as the Boltzmann constant)<sup>1</sup> and  $h$  (the Planck constant) which appear in his equation of radiation entropy, together with the speed of light in

vacuum  $c$  and the gravitational constant  $G$ ,<sup>2</sup> could be used as

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[fundamental constants] to define units for the length, mass, time and temperature, which are independent of special bodies or substances, keep their significance for all times and for all, including extra-terrestrial and non-human civilisations, and can therefore be called "natural units of measurement".

— Max Planck [1], p. 121.  
*(quotation translated from the original German text)*

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At that time, the centimetre–gram–second (CGS) system of units was the predominant system used for scientific purposes. The CGS was superseded by the metre–kilogram–second (MKS) system, which in turn was extended (MKSA, the A standing for ampere) and finally replaced by the International System of Units (SI), the modern form of the metric system. The SI was created in 1960 and has become the universal system of units and the standard measurement language for trade and science.

Since 1971, the SI consists of seven base units which are the **metre** (the unit of length with the symbol m), the **kilogram** (mass, kg), the **second** (time, s), the **ampere** (electric current, A), the **kelvin** (thermodynamic temperature, K), the **mole** (amount of substance, mol), and the **candela** (luminous intensity, cd). In 2019, the SI made a decisive step forward. From that date, the magnitudes of all SI units have been defined by declaring exact numerical values for seven defining constants (see Table 1). These defining constants are the speed of light in vacuum  $c$  (defining constant for the meter,  $c \rightarrow \text{m}$ ), the Planck constant  $h$  ( $h \rightarrow \text{kg}$ ), the hyperfine transition frequency of caesium  $\Delta\nu_{\text{Cs}}$  ( $\Delta\nu_{\text{Cs}} \rightarrow \text{s}$ ), the elementary charge  $e$  ( $e \rightarrow \text{A}$ ), the Boltzmann constant  $k_B$  ( $k_B \rightarrow \text{K}$ ), the Avogadro constant  $N_A$  ( $N_A \rightarrow \text{mol}$ ), and the luminous efficacy  $K_{\text{cd}}$  ( $K_{\text{cd}} \rightarrow \text{cd}$ ). It is quite remarkable that three of these defining constants happen to be those that had been advised more than a century before by Planck.

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<sup>1</sup> For the sake of consistency with the rest of the document, we have adapted several historical formulas using today's most commonly accepted symbols.

<sup>2</sup> Newtonian constant of gravitation,  $G = 6.67408 \times 10^{-11} \text{ m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^{-2}$  (2018 CODATA recommended value).

**Table 1:** The seven defining constants of the International System of Units (SI).

Defining constant	Symbol	Numerical value	Unit
speed of light in vacuum	$c$	299 792 458	$\text{m}\cdot\text{s}^{-1}$
Planck constant <sup>a</sup>	$h$	$6.626\,070\,15 \times 10^{-34}$	J.s
hyperfine transition frequency of caesium-133 ( $^{133}\text{Cs}$ )	$\Delta\nu_{\text{Cs}}$	9 192 631 770	$\text{s}^{-1}$
elementary charge <sup>a</sup>	$e$	$1.602\,176\,634 \times 10^{-19}$	C
Boltzmann constant <sup>a</sup>	$k_{\text{B}}$	$1.380\,649 \times 10^{-23}$	$\text{J}\cdot\text{K}^{-1}$
Avogadro constant <sup>a</sup>	$N_{\text{A}}$	$6.022\,140\,76 \times 10^{23}$	$\text{mol}^{-1}$
luminous efficacy of 540 THz radiation <sup>b</sup>	$K_{\text{cd}}$	683	$\text{lm}\cdot\text{W}^{-1}$

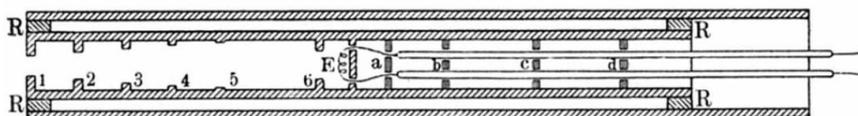
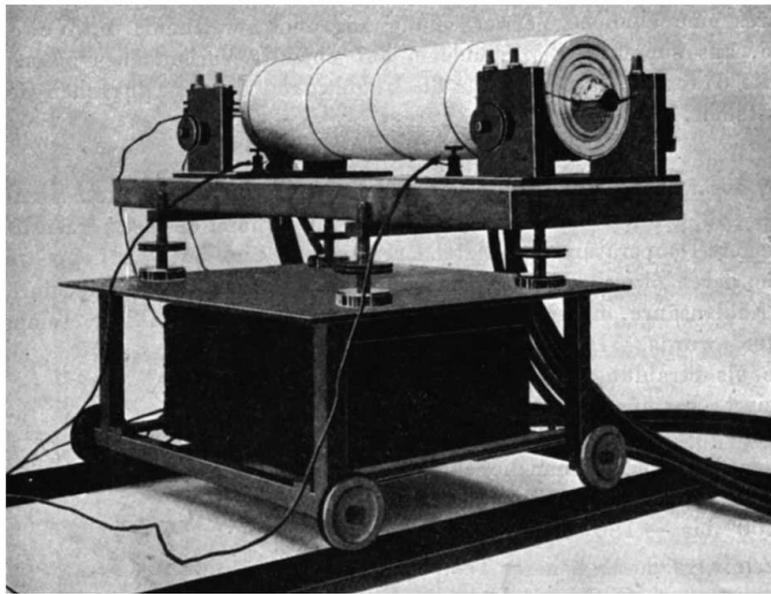
- a) These numerical values have been fixed to their best estimates, as calculated from the 2017 CODATA special adjustment.
- b) Using the relation  $\lambda = c/\nu$  and considering a monochromatic radiation of frequency  $\nu = 5.4 \times 10^{14}$  Hz, we find  $\lambda \approx 555.17$  nm for the corresponding wavelength of the light source (green).

### 3. Blackbody radiation and the birth of quantum mechanics

To understand what motivated Planck to investigate the radiation entropy mentioned above, let's go back to the 19<sup>th</sup> century and examine one object that captivated Planck and so many other renowned physicists for

several decades. In 1859, Gustav Kirchhoff coined the term “blackbody” to describe that object: a body that perfectly absorbs all thermal radiation falling upon it [2]. As is well known, black surfaces absorb light, they also absorb the greatest amount of thermal radiation. But there is another phenomenon associated with absorption which, in scientific terms, can be translated into the following statement: a surface in thermal equilibrium has an equal capacity of absorption and emission of thermal radiation; this relationship between absorption and emission is known as Kirchhoff’s law of thermal radiation. Thus, a blackbody emits radiations whose characteristics are independent of the nature of the source of radiation and depend solely on its temperature. To demystify the blackbody, one can consider that solar radiation falling on the Earth closely approaches that of a blackbody in thermal equilibrium at 5777 K ( $\approx 5500$  °C), as we shall see later. The importance of blackbody radiation is now obvious, as it is crucial for the understanding of thermal radiation and its laws.

From a practical perspective, in order to build a blackbody and be able to study it, one has to heat a cavity to a uniform temperature and allow the radiation to escape through a small aperture. As Kirchhoff had imagined in 1859, such a black cavity radiator is very close to an ideal blackbody. Yet, although simple in appearance, it was not until the close of the 19<sup>th</sup> century that a truly blackbody was designed at



**Figure 1:** The electrical glowing blackbody designed by O. Lummer and F. Kurlbaum in 1898 [2]. Current heats the filament located in a tube inside the cylinder to a fixed temperature, giving rise to blackbody radiation inside that cylinder. The spectrum of this radiation is observed through the hole found at one end along the axis of the cylinder. With a current of about 100 A, temperatures of about 1500 °C (1773 K) could be attained.

the Physikalisch – Technische Reichsanstalt (PTR) in Berlin (see Figure 1). There, blackbody radiation was a lively research topic for both experimental and theoretical physicists for two complementary reasons:

1. Practical (metrology) – The search for better standards (*e.g.*, absolute temperature scales), and in particular for a reliable standard for the radiation of light (radiometry).
2. Theoretical (radiation laws) – The construction of black cavities closely approaching blackbody radiation opened up a path to investigate the exact nature of radiation processes.

The apparatuses developed at the PTR meant great progress for radiation measurements. Experimental physicists could verify with precision measurements a law which had been empirically found by Joseph Stefan in 1879 and theoretically derived by Ludwig Boltzmann in 1884. The Stefan–Boltzmann law states that the radiant emittance,  $M_e$ , of a blackbody is proportional to the fourth power of its thermodynamic temperature  $T$ :

$$M_e = \sigma T^4 \quad [\text{W}\cdot\text{m}^{-2}] \text{ or } [\text{kg}\cdot\text{s}^{-3}] \quad \text{Eq. 1}$$

The constant of proportionality  $\sigma$  is called the Stefan–Boltzmann constant. Today, it can be calculated exactly from the SI defining constants introduced in Table 1:

$$\sigma = \frac{2\pi^5 k_B^4}{15c^2 h^3} \quad [\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-4}] \text{ or } [\text{kg}\cdot\text{s}^{-3}\cdot\text{K}^{-4}] \quad \text{Eq. 2}$$

$$\sigma = 5.670\,374\,419 \dots \times 10^{-8} \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-4}$$

They could also conduct an experimental proof of Wien's displacement law that had been discovered by Wilhelm Wien. Wien's displacement law states that the blackbody radiation curve for different temperatures will peak at wavelengths that are inversely proportional to the temperature. When considering the spectral radiance of blackbody radiation per unit wavelength ( $L_{e,\Omega,\lambda}$ ), it is found that it peaks at the wavelength:

$$\lambda_{\text{pk}} = \frac{\sigma_w}{T} \quad [\text{m}] \quad \text{Eq. 3}$$

The constant of proportionality  $\sigma_w$  is called Wien's displacement constant. It can be calculated exactly by solving a transcendental equation. Using the SI defining constants introduced in Table 1, an approximate value is:

$$\sigma_w = \frac{hc}{4.965\,114\,231\,74\,k_B} \quad [\text{m}\cdot\text{K}] \quad \text{Eq. 4}$$

$$\sigma_w = 2.897\,771\,955 \dots \times 10^{-3} \text{ m}\cdot\text{K}$$

More importantly, they were also able to test Wien distribution law of thermal radiation (now known as Wien's approximation). Using our current knowledge,<sup>3</sup>

this law may be written in terms of the spectral energy density as a function of frequency  $\nu$ :

$$u_\nu(\nu, T) = \frac{8\pi h \nu^3}{c^3} e^{-\frac{h\nu}{k_B T}} \quad \begin{matrix} [\text{J}\cdot\text{m}^{-3}\cdot\text{Hz}^{-1}] \\ \text{or } [\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}] \end{matrix} \quad \text{Eq. 5}$$

Alternatively, Wien's approximation can be written in terms of the spectral energy density as a function of wavelength  $\lambda = c/\nu$ :

$$u_\lambda(\lambda, T) = \frac{8\pi hc}{\lambda^5} e^{-\frac{hc}{\lambda k_B T}} \quad \begin{matrix} [\text{J}\cdot\text{m}^{-3}\cdot\text{m}^{-1}] \\ \text{or } [\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-2}] \end{matrix} \quad \text{Eq. 6}$$

The decisive contribution of the PTR team came from the tremendous refinement of their measurements at longer wavelengths. Indeed, the investigations revealed significant deviations from Wien's theoretical radiation at longer wavelengths. Conversely, a law that had been proposed earlier by John W. Rayleigh proved valid on long wavelengths but failed dramatically on short wavelengths (a divergence that would be coined the "ultraviolet catastrophe" by Paul Ehrenfest in 1911). This law, today known as the Rayleigh–Jeans law, can be obtained using only arguments from "classical" physics:

$$u_\nu(\nu, T) = \frac{8\pi k_B T \nu^2}{c^3} \quad \begin{matrix} [\text{J}\cdot\text{m}^{-3}\cdot\text{Hz}^{-1}] \\ \text{or } [\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}] \end{matrix} \quad \text{Eq. 7}$$

$$u_\lambda(\lambda, T) = \frac{8\pi k_B T}{\lambda^4} \quad \begin{matrix} [\text{J}\cdot\text{m}^{-3}\cdot\text{m}^{-1}] \\ \text{or } [\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-2}] \end{matrix} \quad \text{Eq. 8}$$

These contradictory results were presented by H. Rubens and F. Kurlbaum to the Prussian Academy in October 1900 and published one year after [3].

This work is considered to be the turning point in theoretical research on blackbody radiations. Indeed, it turns out that Rubens was a friend of Planck, as reported by the science historian A. Pais [4]. In the course of a conversation, Rubens mentioned to Planck that he had found  $u_\lambda(\lambda, T)$  to be proportional to  $T$  for large wavelengths, *i.e.* in the infrared. In fact, it didn't take Planck long time to find a solution satisfying both Eq. 6 at short wavelengths and Eq. 8 at long wavelengths. Through interpolation, he found:

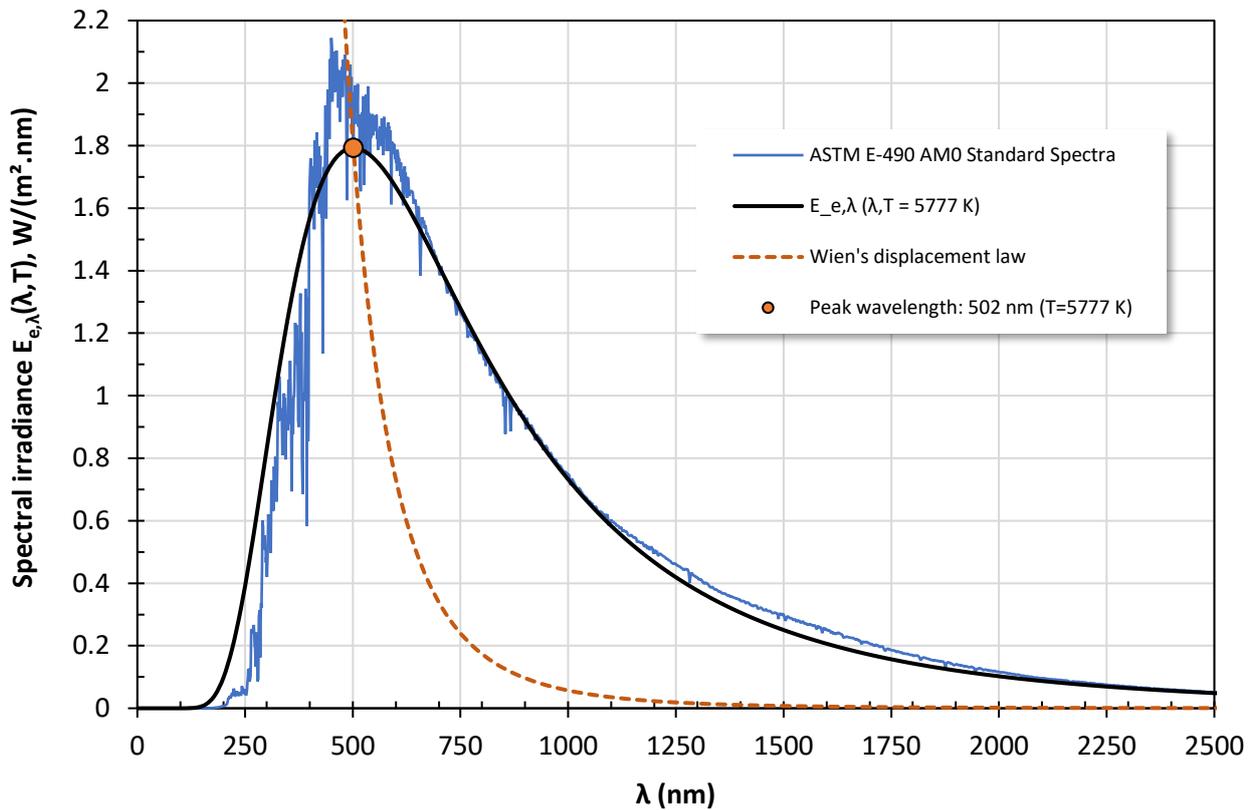
$$u_\lambda(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \quad \begin{matrix} [\text{J}\cdot\text{m}^{-3}\cdot\text{m}^{-1}] \\ \text{or } [\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-2}] \end{matrix} \quad \text{Eq. 9}$$

for the spectral energy density as a function of wavelength. Or, when expressed in terms of frequency instead of wavelength, using Eq. 5 and Eq. 7:

$$u_\nu(\nu, T) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{k_B T}} - 1} \quad \begin{matrix} [\text{J}\cdot\text{m}^{-3}\cdot\text{Hz}^{-1}] \\ \text{or } [\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}] \end{matrix} \quad \text{Eq. 10}$$

<sup>3</sup> Of course, photon energy ( $\varepsilon = h\nu$ ) didn't appear in this form in Wien's original equation since it was Planck who introduced energy

quanta (see Appendix) and Einstein who introduced the concept of light quanta (see section 4).



**Figure 2:** Solar radiation spectrum is compared with a 5777 K blackbody ( $\approx 5500\text{ }^{\circ}\text{C}$ ). ASTM E-490 represents solar spectral irradiance above the atmosphere. For this temperature of the blackbody, Wien's displacement law predicts a peak wavelength around 500 nm.

These two equations appear exactly in this form in Planck's famous paper "On the law of distribution of energy in the normal spectrum" published in 1901 [5].

Planck's discovery is by no means limited to an interpolation of experimental data. This was actually the starting point of the most heroic period of his life. Blackbody radiation involved an inescapable break with classical physics. As a physicist, he had to find a rational explanation. His law had to derive from a fundamental principle. He succeeded to give a physical explanation, but in order to do so he had to make the following hypothesis: radiation energy is found in the form of discrete energy elements  $\varepsilon$  – *i.e.*, quantized energy – that are proportional to the frequency  $\nu$ :

$$\varepsilon = h\nu \quad [\text{J}] \text{ or } [\text{kg}\cdot\text{m}\cdot\text{s}^{-2}] \quad \text{Eq. 11}$$

For further details, readers will find in the Appendix a brief overview of the masterful demonstration that led Planck to the postulate of energy quanta.

To conclude this section on blackbody radiation, we show in Figure 2 the solar radiation spectrum as

compared to a 5777 K blackbody (about  $5500\text{ }^{\circ}\text{C}$ ). The ASTM E-490 solar spectral irradiance is based on a collection of data recorded above the atmosphere. Its integrated spectral irradiance has been made to conform to the value of the solar constant accepted by the space community, which is  $1366.1\text{ W/m}^2$ . The spectral irradiance  $E_{e,\lambda}$  is calculated from the spectral energy density  $u_{\lambda}$  given in Eq. 6:

$$E_{e,\lambda}(\lambda, T) = c \frac{\Omega_{\text{Sun}}}{4\pi} u_{\lambda}(\lambda, T) \quad [\text{W}/(\text{m}^2\cdot\text{m})] \quad \text{Eq. 12}$$

with  $\Omega_{\text{Sun}} \approx 6.807 \times 10^{-5}\text{ sr}$ , the solid angle of the Sun as seen from Earth.<sup>4</sup> Although the Sun is not a perfect blackbody, we can see a relatively good correspondence with the 5777 K blackbody. According to Wien's displacement law (Eq. 3), the peak wavelength of the 5777 K blackbody is around 502 nm:

$$\begin{aligned} \lambda_{\text{pk}} &= \sigma_w / (5777\text{ K}) \\ &\approx 5.016 \times 10^{-7}\text{ m} \\ &\approx 502\text{ nm} \end{aligned}$$

<sup>4</sup> The Sun as seen from Earth has an average apparent angular diameter of  $2\theta_{\text{Sun}} \approx 0.5334^{\circ}$ . The corresponding solid angle is  $\Omega_{\text{Sun}} = 2\pi (1 - \cos(\theta_{\text{Sun}}))$ , expressed in steradian [sr].

#### 4. Photoelectric effect

After 1901, nothing further happened in quantum mechanics until Albert Einstein proposed the light quantum hypothesis in 1905 [2]. Einstein's greatest strength lay in looking down through ideas from the scientific literature, than to draw together these isolated insights into consistent theories [2]. This was of fitting form the framework of his paper "On a heuristic point of view concerning the generation and conversion of light" [2], [3]. This is how he came up with the first quantum theory of radiation. At this point, it should be noted that the word "photon" – which denotes the particle nature of light – did not appear until 1926, after the wave-particle duality had been clarified.

Planck had proposed Eq. 12 in 1900 but it was only an ad-hoc assumption. As Planck considered, it was assumed to be a mathematical artifact. Meanwhile, Philipp Lenard was working on "cathode ray" and encountered various difficulties when attempting to explain photoelectric phenomena, that is the emission of electrons (photoelectrons) after light hits a material. Lenard found that the electron energy showed "not the slightest dependence on the light intensity" [2]. On the other hand, he could observe that photoelectron energy did increase with the frequency  $\nu$  of monochromatic light.

Einstein then proposed the following picture for the photoelectric effect: A light quantum of frequency  $\nu$  transfers all its energy to a single electron, independently of the presence of other light quanta. The electron can suffer energy loss before it reaches the surface. When ejected from the surface of the material, electron energy is found to increase linearly and to reach  $E_{\text{max}}$  in those cases where this energy loss is zero. He translated the photoelectric effect into the following equation (in modern notation):

$$E_{\text{max}} = h\nu - \phi \quad (4.12)$$

where  $\phi$  is the work function of the material, i.e. the energy needed to escape the surface. Eq. 12 explains Lenard's observation of the electron energy being independent of the light intensity. With this equation, Einstein made several strong predictions:

- 1) linear dependence of  $E_{\text{max}}$  with  $\nu$
- 2) the slope  $h$  is the Planck constant, it is thus independent of the material
- 3) the work function is a material dependent property

4) one can define  $\lambda_{\text{th}} = c/\nu$ , a threshold frequency of light below which no photoelectric effect is observed

As an illustrative example, let's consider light incident on a clean (Ag) plate. The work function of silver,  $\phi_{\text{Ag}}$  is around 4.2 eV (electron-volt):

$$\begin{aligned} \phi_{\text{Ag}} &= 4.2 \text{ eV} \\ &= 4.2 \times 1.602 \times 10^{-19} \text{ J} \approx 6.73 \times 10^{-19} \text{ J} \\ &= 6.73 \times 10^{-19} \text{ J} \end{aligned}$$

The threshold wavelength,  $\lambda_{\text{th}}$ , above which no photoelectric effect is observed is:

$$\begin{aligned} \lambda_{\text{th}} &= \frac{c}{\nu} = h c / \phi_{\text{Ag}} \\ &= 2.88 \times 10^{-7} \text{ m} \\ &= 288 \text{ nm} \end{aligned}$$

The threshold wavelength is in the deep ultraviolet, in other words, nothing happens when visible light hits clean, visible light does not have enough energy to free an electron from silver.

#### 5. Semiconductor photonic devices

The discovery of the photoelectric effect and the advances in quantum physics were a prerequisite to the construction of semiconductor photodiodes – commonly referred to as photodiodes – and light-emitting diodes (LEDs). We know from quantum physics that the energy of an electron in an atom is quantized. In a solid, the electrostatic interaction results in the formation of energy bands. These energy bands can overlap, as is the case in metals. However, there are certain materials (referred as semiconductors) where the interaction between atoms and their valence electrons (outer shell electrons) results in two very close but distinct energy bands. They are called the valence band (energy  $E_v$ ) and the conduction band (energy  $E_c$ ) and are separated by an energy gap, or energy "barrier"  $E_g$

$$E_g = E_c - E_v \quad (4.14)$$

This barrier prevents forbidden electron energies in the material. As a result, semiconductors have a very distinctive electrical characteristic: that charge depending on the environment. This can then come to the fact that their conductive behaviour lies between that of a conductor and an insulator. For instance silicon (Si) metal – a pure or "intrinsic" semiconductor – is an insulator at room temperature but becomes slightly conductive when heated. Of course, there are other more effective ways of changing semiconductor conductivity, for instance by using light, an electric current, a magnetic field or an electric field.

<sup>2</sup> The electron-volt [eV] is a convenient alternative to the joule [J]. It is obtained from its definition (charge,  $e$ ) [2],  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ , from the [2]–[2.10].

Table 2. Typical energy band gap of some semiconductor materials

Material	Energy bandgap <sup>a</sup> ( $E_g$ ) in eV	Cutoff wavelength ( $\lambda_c$ ) in nm
Aluminum Nitride (AlN)	6.2 eV, direct	200 nm
Gallium Nitride (GaN)	3.4 eV, direct	360 nm
Gallium Phosphide (GaP)	2.26 eV, indirect	550 nm
Silicon (Si)	1.12 eV, indirect	1100 nm
Germanium (Ge)	0.67 eV, direct	1800 nm
Indium Nitride (InN)	0.65 eV, direct	1900 nm

a) Indirect bandgap semiconductors, such as silicon, cannot be directly excited to make LEDs.

Doping, i.e. the introduction of foreign atoms species (donor/acceptor), is another way to locally change a semiconductor conductivity. It is the basic process for the manufacture of the so-called "hetero" semiconductor devices. Current conductivity in a doped semiconductor is enhanced due to mobile charge carriers, which are either electrons or electron "holes" (the lack of electrons). When a doped semiconductor contains acceptor holes, it is called a p-type material (p stands for positive electric charge) when it carries across the electrons, it is called an n-type material (negative). A p-n junction is formed when the n- and p-type semiconductors have intimate contact. The p-n junction is the building block of semiconductor devices: a diode, a photodiode and a light-emitting diode (LED) can be made from a single p-n junction.

At the p-n junction, electrons and holes diffuse to recombine with each other. This creates a region without charge carriers, a depletion. At the depletion, a built-in electric field is obtained which acts as a barrier to the movement of electrons. This implies that a voltage at least equal to the potential barrier,  $V_{bi}$ , must be applied across the p-n junction in order for the electrons to move through this electric field (E), i.e. a photonic device, when an electron jumps this energy, it can result either in the emission or in the absorption of a photon:

$$\text{electron} + \text{hole} = \text{photon}$$

In a photodiode, the absorption of a photon results in a free electron-hole pair, that is the creation of an electron in the conduction band and the creation of a hole in the valence band. Whether a photodiode or an LED, the photoelectron or the excited photon must have an energy equal to  $E_g$ , the energy difference between the conduction band electron and the valence band hole that participated in the process (3). As a first approximation, we may write:

$$h\nu = E_g \quad (4)$$

Energy  $h\nu$  may also be written as a function of the voltage  $V$  across the p-n junction (see also footnote 2):

$$h\nu = eV \quad (5)$$

Due to the conservation of energy, the electron energy  $eV$  equals the photon energy  $h\nu$  (see Eq. (5)):

$$eV = E_g \quad (6)$$

Beyond activation, the voltage  $V$  across the device is about the same as the potential barrier  $V_{bi}$ , thus:

$$V_{bi} = \frac{E_g}{e} \quad (7)$$

Combining these equations, we finally find the characteristic wavelength  $\lambda_c$ :

$$\lambda_c = \frac{hc}{E_g} \quad (8)$$

This wavelength is known as the cutoff wavelength for photodiodes (10), while it approximates the peak emission wavelength of an LED (3). For example, in the case of silicon, the bandgap energy is around 1.12 eV, so the cutoff wavelength of an Si photodiode is around 1100 nm (see Table 2). This means that an Si photodiode can be used to detect photons whose wavelength is lower than 1100 nm.

As we are concerned with the spectral distribution of LEDs, an important remark must be given concerning the approximation made at Eq. (8). Although the material bandgap  $E_g$  is in the ability of the material bandgap  $E_g$ , its distribution depends on the width of the associated energy bands and on the statistical distribution of free carriers within these bands. In concrete terms, since LEDs are semiconductor materials that have energy bands instead of discrete energy levels as in the case of gases, free carrier transition between these energy bands allows photon emission in a relatively wide wavelength window (9). For a given peak emission wavelength, an LED will show a relatively broader emission spectrum as compared to that achievable with a corresponding gas-discharge lamp. On the other hand, LED spectrum is well-determined as opposed to the continuous radiation of gas-discharge lamps. This is illustrated in Figure 2 which compares the spectral power distribution (SPD) of an ultraviolet (UV) "500 nm" (in LED) with that of a mercury-vapor lamp (Hg).

## 5. Photodiode responsivity

From sections 4 and 5, it follows that when the wavelength is too long and the photon energy is too low, the response of a photodiode will drop to zero if the necessary condition  $h\nu > E_g$  is not satisfied. Let's see what happens when this condition is satisfied. The absorbed photons create photoelectrons that can be

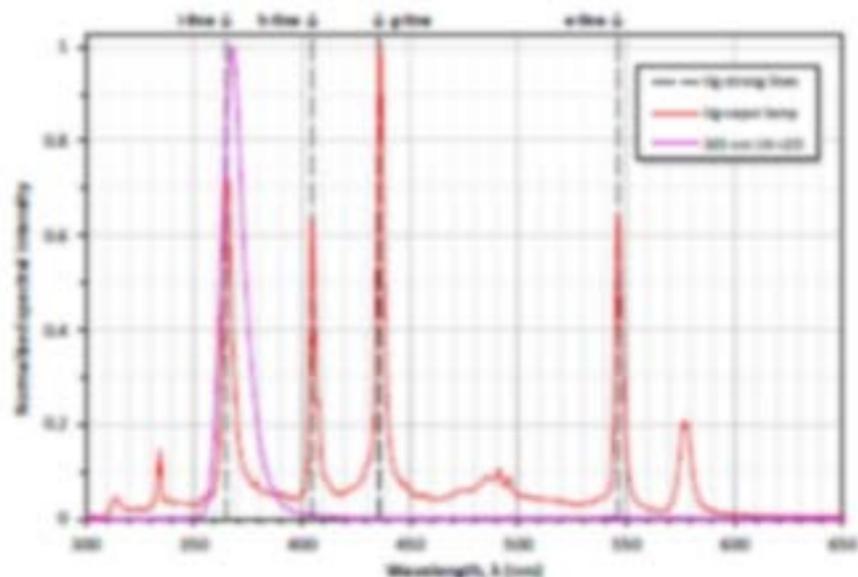


Figure 3. Spectral power distribution of a “500 nm” violet LED lamp is compared with that of a mercury vapor lamp. Both spectra were captured with an extended-range spectrometer (F4680-2-001-01, Ocean Insight, Inc.)

collected and give rise to a photocurrent,  $I_{ph}$ . From the definition of the ampere,  $[I] = [C/s]$ , the number of electrons collected per second is  $I_{ph}/e$ . The total optical power (or radiant flux) incident on the photodiode is  $\Phi_e$ , and is measured in watts,  $[W] = [J/s]$ . Similarly to what we did in section 1, we use the subscript  $v$  for the radiant flux per unit wavelength (spectral flux),  $\Phi_{e,v}$ , in units of watts per meter,  $[W/m] = [J/s^2/m]$  or  $[W \cdot m^{-1}]$ . With this formalism, we can now express the number of photons received per second for a given wavelength,  $\Phi_{e,v}(\lambda)$ .

Not all the photons are absorbed and converted into photocurrent. The efficiency of this conversion is measured by the quantum efficiency ( $\mathcal{Q}$ ) of the photodiode,  $\mathcal{Q}_{ph}$ :

$$\mathcal{Q}_{ph} = \frac{\text{No. generated electron-hole pairs}}{\text{No. incident photons}} \quad \text{Eq. 20}$$

This expression can be rewritten as:

$$\mathcal{Q}_{ph} = \frac{I_{ph}/e}{\Phi_{e,v}(\lambda)} = \frac{I_{ph}}{e \Phi_{e,v}(\lambda)} \quad \text{Eq. 21}$$

The ratio  $I_{ph}/\Phi_{e,v}$  is called the spectral responsivity  $\mathcal{R}$  of a photodiode. It characterizes the photodiode

performance in terms of photocurrent per incident optical power at a given frequency (spectral flux):

$$\mathcal{R}(\lambda) = \frac{I_{ph}(\lambda)}{\Phi_{e,v}(\lambda)} \quad [A/W] \quad \text{Eq. 22}$$

From the definition of  $\mathcal{Q}$  given in Eq. 21, it follows that:

$$\mathcal{R} = \mathcal{Q}_{ph} \frac{e}{h\nu} = \mathcal{Q}_{ph} \frac{hc}{\lambda h\nu} \quad [A/W] \quad \text{Eq. 23}$$

Because  $\mathcal{Q}$  depends on the wavelength,  $\mathcal{R}$  is therefore clearly dependent on the wavelength.

We can now give the responsivity of a photodiode as a function of the wavelength  $\lambda$ , considering the cutoff wavelength  $\lambda_c$  given in Eq. 19:

$$\begin{cases} \mathcal{R}(\lambda < \lambda_c) = \mathcal{Q}_{ph} \frac{hc}{\lambda h\nu} \\ \mathcal{R}(\lambda \geq \lambda_c) = 0 \end{cases} \quad \text{Eq. 24}$$

The characteristic  $\mathcal{R}(\lambda)$  represents the spectral response of the photodiode and can be found in the manufacturer's datasheet. Figure 4 shows the typical responsivity of a silicon photodiode as compared with its ideal theoretical model. In the ideal case, the responsivity increases linearly with the wavelength and then suddenly drops at the cutoff wavelength  $\lambda_c$ . In

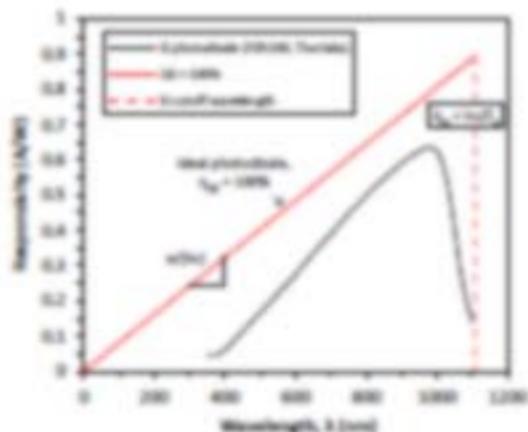


Figure 6. The spectral response of an ideal photovoltaic quantum efficiency ( $Q = 100\%$ ) is compared with that of a commercial silicon photovoltaic (model S1200, Toshiba, Inc.)

spectra ( $Q = 100\%$ ) and the responsivity curve is found to be below the ideal curve. This being said, one should note that the spectral response of silicon photovoltaic covers the entire visible spectrum. Furthermore, its linearity is remarkable for wavelengths in the visible range, which makes it a suitable candidate for visible light radiometry.

### 7. Spectral power distribution of a light-emitting diode

We concluded section 5 by pointing out that, due to the width of the energy bands and to the statistical distribution of free carriers, the spectral power distribution (SPD) of LEDs is a relatively wide curve around a peak emission wavelength. As can be seen in Figure 5, the SPD may be approximated as an asymmetric gaussian curve. This asymmetry is more or less pronounced and depends on the composition of the semiconductor material. Thanks to the knowledge disseminated so far, a more in-depth interpretation of the SPD is now at hand.

To describe LED emission spectrum, Würfel proposed a generalization of Planck's law of radiation [21], [22], [23]. By introducing a nonzero "chemical potential" of photons, he showed that the light emitted by LEDs can be well described by a thermodynamic theory extending Planck's law to luminescent radiation. Using the relation introduced in section 3, the spectral energy density as a function of photon frequency reads as follows:

$$u_{\omega}(\nu, T) = \frac{h\nu^3}{4\pi^3 c^3} \frac{e^{h\nu - \mu}}{e^{h\nu - \mu} - 1} \quad (9.25)$$

with Eq. (2). Because a blackbody is an ideal object that has perfect absorption, its surface absorptivity is always 1, so  $a_{\omega}(\nu) = 1$ . Next, blackbody relation describes the state of light in which the chemical potential is zero [21], so  $\mu = 0$ .

In artificial lighting devices such as LEDs, light is produced with a non-zero chemical potential by using chemical equilibrium with the excited matter. Contrary to a blackbody, LED light has a temperature not far from room temperature, and its chemical potential is greater than zero,  $\mu > 0$ . The temperature  $T$  is that of the electron-hole gas, which is equal to the semiconductor junction temperature. The chemical potential is equal to that of the electron-hole pair, which is determined by the voltage  $V$  across the p-n junction:  $\mu = eV$  [22]. In semiconductors, the electrochemical potential,  $\mu$ , is known as the quasi-Fermi level splitting.

Now, we observe that Eq. (25) seems to diverge at  $h\nu = \mu$ , which of course doesn't happen in practice. This apparent inconsistency is resolved by noting that the energy-dependent factor  $u_{\omega}(\nu)$  holds information about carrier density of states. In an idealized LED,  $u_{\omega}(\nu)$  is a step function: photons with energy smaller than the bandgap energy cannot be absorbed by generating electron-hole pairs, resulting in  $u_{\omega}(h\nu < \mu_g) = 0$ , whereas all photons with energy higher than the bandgap energy are fully absorbed,  $u_{\omega}(h\nu > \mu_g) = 1$  [22]. From these considerations, Würfel concludes that, for LEDs, the  $-1$  in the denominator of Eq. (25) can be neglected [21], [22]. As a result, Eq. (25) may be approximated by:

$$u_{\omega}(\nu, T) = u_{\omega}(\nu) \frac{h\nu^3}{4\pi^3 c^3} e^{-\frac{h\nu - \mu}{k_B T}} \quad (9.26)$$

This relation can be regarded as Wien's generalized law of radiation applied to LEDs (see Eq. 9 for comparison). Light emission above the bandgap energy can be thought of as Planckian radiation exponentially enhanced by diode voltage [22].

Eq. (26) predicts that the light emitted by a LED is fully described by the absorptivity, the applied voltage and the junction temperature. Absorptivity is definitely the most complex part of this equation as it depends on the internal composition of the p-n junction (e.g., optical

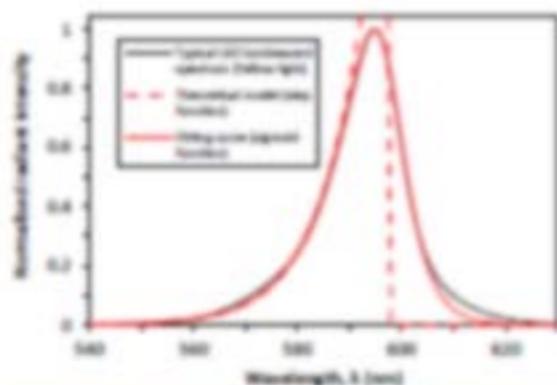


Figure 5. Spectral power distribution (SPD) of an LED. The simplified model uses a step function. A reasonably good fitting is obtained using a sigmoid function for the electron-hole distribution of states. The measured SPD is that of a commercial yellow LED. It was measured with an extended-range spectrometer (FLAME-3-SPS-4), (these might, be.)

distribution of the doping) rather than the unsmoothed step function, it seems reasonable to approximate the discontinuity function by an "S" shaped curve, a sigmoid function. Many scientific works dedicated to the modeling of electroluminescence spectra are based on Wien's equation or on an historical model that had been derived by van Roosbroeck and Shockley [30], [31], [32], [33]. One of the interests of these models is that they can extract parameters that have physical significance. In this regard, we mention the work of Vahedi et al. who have proposed different sigmoid-based models for the effective electron-hole SPD depending on the nature of the semiconductor (semiconductor III-V and blue nitride LEDs) [34]. In Figure 5, we show the typical SPD of a yellow LED and compare it with the theoretical model (Eq. 26). The sigmoid function (2) used for the fitting is a logistic curve with equation

$$f(x) = \frac{1}{1 + e^{-\frac{x - \lambda_0}{L}}} \quad (27)$$

where  $L$  is a scaling factor, wavelength  $\lambda_0$  is the sigmoid midpoint, and  $e^{-1}$  defines the steepness of the sigmoid. In this simple fitting,  $L_{sp}$  was chosen so that  $\sigma_f = \lambda_0/L_{sp}$ . By through parameter  $\sigma_f$ , it is actually both the spread and the steepness of the SPD that are controlled.

### 5. Radiometric measurement of LEDs with a photodiode

In section 7, we have seen that a LED's electroluminescence spectrum could be modeled as the product of a Maxwell-Boltzmann distribution by the

density of states of electron-hole in the p-n junction. Thus, it would theoretically be possible to obtain the spectrum of LEDs with the help of physically based parameters. Although this approach is elegant, it comes at a great practical difficulty. First and foremost, the fact that the composition of LED semiconductor is hardly ever disclosed.

On the other hand, these LEDs are supplied with detailed technical specifications, in particular concerning their typical SPD. Therefore, we can use mathematical models that closely fit to the SPD but have no physical significance. By exploiting Eq. 26 and from the observation of LED spectra, it can be seen that approximation by a sum of Gaussian distributions is a possible choice. It is indeed an appropriate choice, all the more so as it enables more complete spectra to be modeled. Here, the spectrum of white LEDs comes to mind. The fitting function  $g(\lambda)$  writes as follows:

$$g(\lambda) = \sum_{i=1}^n A_i e^{-\frac{(\lambda - \lambda_i)^2}{2\sigma_i^2}} \quad (28)$$

where  $A_i$ ,  $\lambda_i$  and  $\sigma_i$  are the fitting parameters for a single peaked SPD spectrum, assuming things can usually be obtained with  $n \geq 2$ . In what follows, for the sake of clarity, the denominators are made for  $n = 2$ .

Let's consider again the UV-LED whose spectrum was shown in Figure 3 and for which we want to measure the radiant flux in rougher experimental conditions. Here, the SPD was measured with a spectrometer but it could just as well have been extracted from the LED datasheet. Using the algorithm that is provided in Table 5, we can extract the fitting parameters from function  $g(\lambda)$  in Eq. 28. The result is shown in Figure 6. As a first approximation, the SPD is modeled assuming a gaussian distribution of the spectral flux,  $\Phi_{e,sp}(\lambda)$ :

$$\Phi_{e,sp}(\lambda) = A_{sp} e^{-\frac{(\lambda - \lambda_{sp})^2}{2\sigma_{sp}^2}} \quad (29)$$

The radiant flux width at half maximum of this gaussian is simply calculated from the standard deviation  $\sigma_{sp}$

$$\text{FWHM} = 2 \sigma_{sp} \sqrt{2 \ln 2} = 2.35482 \sigma_{sp} \quad (30)$$

The radiant flux  $\Phi_e$  is obtained through integration of the spectral flux:

Table 3. The curve-fitter computes a fitting algorithm from raw data of a JSD spectral power distribution.

```

13 k Fitting algorithm: sequential regression with 300 steps
k Data are loaded from a CSV file (e.g., "JSD_spectrum.csv")
k
k 100 samples for "mean-squared value"
14 k The 100 samples of JSD data k and T data arranged in two columns
k Values can be accessed either with k index i,j or a structure xx
clear
15 k Load k and T matrix
data = load('JSD_spectrum.csv');
data = data(:,1);
Tdata = data(:,2);
16 k Define the model. Here, we use a set of Gaussian functions for the fitting
model_fit = fit('sum(gauss)');
= g(1).Peak+G.P1*cos(g(2)) / g(1).T0; ...
= g(2).Peak+G.P1*cos(g(2)) / g(2).T0; ...
= g(3).Peak+G.P1*cos(g(2)) / g(3).T0+T0;
17 k Function to evaluate the model. In this case, we need to provide
k the error function: residual sum of squares (RSS)
RSS_fit = fitg, fit; ...
= g(1).Peak+G.P1*cos(g(2)) / g(1).T0; ...
= g(2).Peak+G.P1*cos(g(2)) / g(2).T0; ...
= g(3).Peak+G.P1*cos(g(2)) / g(3).T0;
k Initial guess
g_init = [1, 100, 0, 0.5, 100, 10, 0.5, 100, 10];
18 k Because this fitting parameters are displayed to the Command Window
fitting_parameters = fitname(model_fit, g_init);
k k graph is displayed
plot(data, data, 'b');
fig = get(gcf);
set(fig, 'Name','JSD', 'Title', ...
'Peak Fitting with a set of Gaussian functions');
hold on
plot(data, fitg(fitting_parameters), data, ...
'r', 'LineStyle', 'd');
xlabel('Wavelength, nm (nm)');
ylabel('Spectral Irradiance, W/m^2/nm (1/nm)');

```

$$e_{\lambda} = \int_{\lambda_1}^{\lambda_2} e_{\lambda}(\lambda) d\lambda = A_{\lambda} A_{\lambda} \sqrt{\lambda} \quad (20)$$

A single gaussian is clearly not a satisfying approximation. The actual spectrum being asymmetrical, the fitting is instead completed with two gaussian functions across the data:

$$\begin{aligned}
 e_{\lambda} &= A_{\lambda} A_{\lambda} \sqrt{\lambda_1} e^{-\frac{(\lambda-\lambda_1)^2}{2\sigma_1^2}} + A_{\lambda} A_{\lambda} \sqrt{\lambda_2} e^{-\frac{(\lambda-\lambda_2)^2}{2\sigma_2^2}} \\
 &= A_{\lambda} A_{\lambda} \sqrt{\lambda_1} + A_{\lambda} A_{\lambda} \sqrt{\lambda_2}
 \end{aligned} \quad (21)$$

We rewrite the model for as:

$$e_{\lambda} = e_{\lambda_1} + e_{\lambda_2} \quad (22)$$

$$\text{where } e_{\lambda_1} = A_{\lambda} A_{\lambda} \sqrt{\lambda_1} \text{ and } e_{\lambda_2} = A_{\lambda} A_{\lambda} \sqrt{\lambda_2}$$

We now introduce the central wavelength,  $\lambda_c$ , which is ideal for characterizing the experimental SPD of LEDs. It is calculated as follows:

$$\lambda_c = \frac{\int_{\lambda_1}^{\lambda_2} \lambda e_{\lambda}(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} e_{\lambda}(\lambda) d\lambda} = \frac{\int_{\lambda_1}^{\lambda_2} \lambda e_{\lambda}(\lambda) d\lambda}{e_{\lambda}} \quad (23)$$

It can be easily shown that Eq. 23 can be rewritten as follows:

$$\lambda_c = \frac{\lambda_1 e_{\lambda_1} + \lambda_2 e_{\lambda_2}}{e_{\lambda_1} + e_{\lambda_2}} \quad (24)$$

This equation clearly shows that the centroid wavelength is analogous to the barycentre of the spectrum.

We want to characterize the (CD) with a photodiode. As we learned in section 5, the responsivity  $R(\lambda)$  of a photodiode is the ratio of the generated photocurrent,  $i_{ph}(\lambda)$ , to the incident spectral flux at a given wavelength,  $\Phi_{\lambda}(\lambda)$ :

$$R(\lambda) = \frac{i_{ph}(\lambda)}{\Phi_{\lambda}(\lambda)} \quad (36)$$

This result is similar to Eq. 22 but involves wavelength-dependent quantities. When integrated in a reformer, the photocurrent delivered by the photodiode is amplified and converted. The output signal,  $i$ , of the reformer is obtained through integration of the responsivity times the spectral flux over the entire bandwidth (WB):

$$i = k \int_{WB} R(\lambda) \Phi_{\lambda}(\lambda) d\lambda \quad (37)$$

where  $k$  is a constant specific to the reformer. As we have seen in Figure 4, the reformer has a non-flat spectral responsivity. However, it can actually be used for metrology if the responsivity can be treated around the (CD) over (WB), at least beyond twice the FWHM. In this case, we have:

$$R(\lambda) = a + b\lambda + c \quad (38)$$

where  $a$  and  $b$  are two constants. At the centroid wavelength, we then find:

$$R(\lambda_c) = a + b\lambda_c + c \quad (39)$$

The slope,  $a$ , can be rewritten as follows:

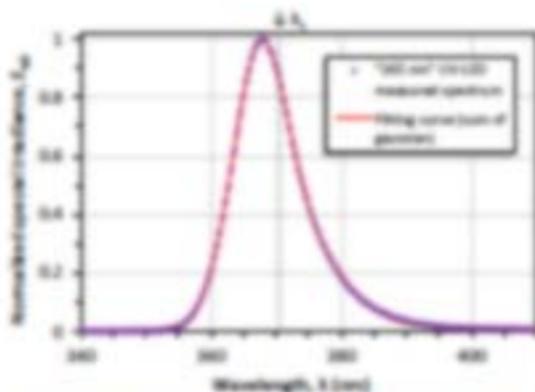


Figure 8: Normalized spectral irradiance of a "100 nm" (10) CD and the fitting curve obtained using the algorithm described in Table 2. The measured (10) is the same as that shown in Figure 2. Note that the centroid wavelength  $\lambda_c$  is slightly shifted with respect to the peak wavelength.

$$a = \frac{R(\lambda_c) - R(\lambda_0)}{\lambda_c - \lambda_0} \quad (40)$$

We deduce the following relation:

$$\begin{aligned} \int_{WB} R(\lambda) \Phi_{\lambda}(\lambda) d\lambda \\ = \int_{WB} (a + b\lambda + c) \Phi_{\lambda}(\lambda) d\lambda \\ = a \int_{WB} \Phi_{\lambda}(\lambda) d\lambda + b \int_{WB} \lambda \Phi_{\lambda}(\lambda) d\lambda \end{aligned} \quad (41)$$

Thus, we have:

$$\begin{aligned} \int_{WB} R(\lambda) \Phi_{\lambda}(\lambda) d\lambda \\ = a I_0 + b I_1 + c I_0 = R(\lambda_c) \Phi_{\lambda_c} \end{aligned} \quad (42)$$

Combining Eq. 42 with Eq. 37, we obtain:

$$i = k \cdot R(\lambda_c) \cdot \Phi_{\lambda_c} \quad (43)$$

This result demonstrates that the output flux  $\Phi_{\lambda_c}$  of a single-peaked (CD) can be properly estimated with a non-flat reformer provided that the photodiode used can be treated around the centroid wavelength  $\lambda_c$  of the (CD). In this case, the calibration parameter to be used is  $R(\lambda_c)$ , the responsivity of the photodiode at  $\lambda_c$ .

Furthermore, there is another important result that stems from the above as it can be straightforwardly shown that:

$$R(\lambda_c) \Phi_{\lambda_c} = R(\lambda_0) \Phi_{\lambda_0} + R(\lambda_1) \Phi_{\lambda_1} \quad (44)$$

Indeed, Eq. 44 implies that a reformer – calibrated for centroid wavelength  $\lambda_c$  – provides the same output signal with same used to measure separately the distinct gaussian spectra at wavelengths  $\lambda_0$  and  $\lambda_1$ , respectively. In other words, the methodology described above can be generalized to the reformer's measurement of multi-peaked (CDs), i.e. broadband spectrum obtained from the combination of several gaussian spectra. In that case, the photodiode must be flat-topped throughout the entire bandwidth.

In Figure 7, we have reproduced the normalized responsivity of a Gallium Phosphide (GaP) photodiode together with the normalized (10) of a multi-peaked (10) CD. In this illustrative example, the (CD) spectrum was fitted with three gaussian curves. It can be seen that the responsivity of GaP does not grow linearly over the entire spectrum of the (CD) (i.e., 380 nm – 420 nm). The solid curve (shaded in

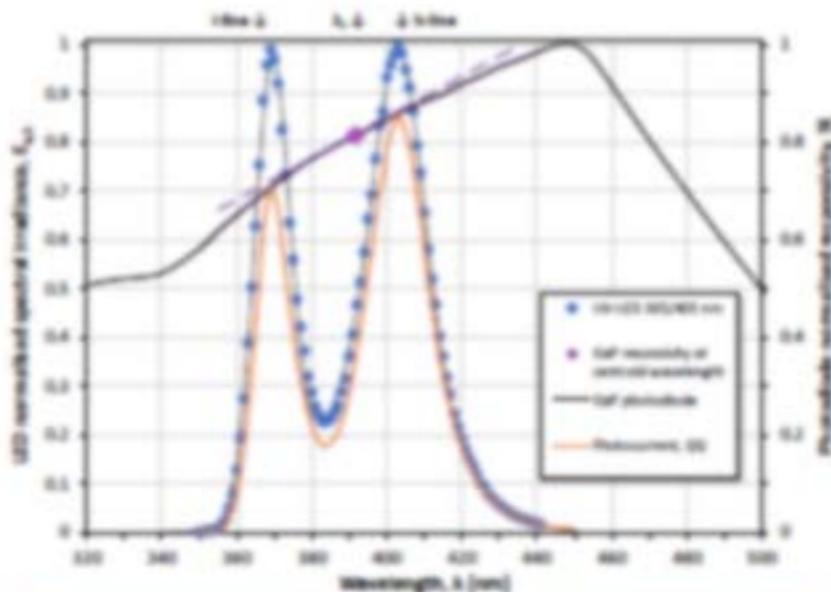


Figure 7. Normalized spectral irradiance of a multi-peak UV-CLED vs. spectral responsivity of Gallium Phosphide (GaP) photodiode. The solid curve (2) is the calculated wavelength-dependent photocurrent. GaP responsivity can be decreased in the near UV range, making GaP semiconductor a suitable radiometric sensor for this UV-CLED.

The graph was calculated as  $E(\lambda) = R(\lambda) \cdot R_{\lambda}(\lambda)$  by data interpolation. Clearly, from Eq. 21, one can immediately see that the output signal of the photodiode is obtained through integration of the latter curve. As demonstrated above (see Eq. 22), the reflect for  $R_{\lambda}$  can directly be retrieved from the radiometer provided that the centroid wavelength  $\lambda_c$  is used for the responsivity  $R(\lambda_c)$ . Through numerical integration of the data displayed in Figure 7, we find that the estimation error is  $\sim 15\%$  when  $\lambda_c$  is used to calculate the responsivity. The reflect for  $R_{\lambda}$  is overestimated by almost  $\sim 12\%$  if the blue peak (390 nm) is used, while it is underestimated by about  $\sim 6\%$  if the blue peak (380 nm) is used. These errors can easily be retrieved if one observes the relative responsivities of GaP at these wavelengths.

The experiments carried out with a spectrometer and a GaP photodiode corroborate the theoretical prediction that the photodiode can be used as a reliable radiometric sensor for the characterization of broadband LEDs. This is needed to the linearity of photodiode responsivity, which must of course be verified throughout the entire spectrum of the LED or group of LEDs of interest. To use a calibrated photodiode as a radiometer for LEDs, the centroid wavelength of its spectrum is then the only

parameter that needs to be known to properly scale the output signal. The premises of such idea can be found in studies conducted by Speiser et al. from the National Institute of Standards and Technology (NIST, USA) [26], [27]. However, these studies focused on single-peaked LEDs and considered the peak wavelength instead of the more suitable centroid wavelength. As a last remark, note that (i) the typical peak wavelength of LEDs is always mentioned in their datasheets; (ii) the centroid wavelength is usually provided for LEDs emitting in the non-visible spectrum (infrared or ultraviolet). One should not use the "dominant wavelength" usually provided for LEDs emitting in the visible spectrum; this is a photometric value that articulates the apparent color, as perceived by the average human eye.

## 6. Conclusion

We began this white paper by emphasizing on the importance of accurate and precise measurements for science and technology. This applies to a GaP diode applicable to radiometric measurement and calibrated the writing of this white paper whose primary aim was to demonstrate the reliability of radiometric measurement

of LEDs using a simple photodiode. The proof can be summarised in two main points:

1. The electroluminescence spectrum of a LED can be approximated by a sum of gaussian curves from which a centroid wavelength  $\lambda_c$  can be derived;
2. By appropriate choice of a photodiode (*i.e.*, with a linearizable responsivity  $\mathfrak{R}(\lambda)$  throughout the entire bandwidth of the LED), its output signal gives a correct radiometric measurement of the LED provided scaling by its responsivity at centroid wavelength,  $\mathfrak{R}(\lambda_c)$ .

This is detailed in section 8 and we could have limited this paper to that section. However, we wanted to take the investigation on LEDs spectra a step further and explain the origin of their asymmetric gaussian-like shape.

One thing leading to another, what we did out of scientific curiosity eventually led us to dig in history of science, with blackbody radiation as the starting point. As we have stressed it in section 3, it was indeed the need for reliable standard for the radiation of light that prompted standardisation institutes to take an interest in blackbody radiation at the end of the 19<sup>th</sup> century. In light of what we have seen throughout this paper, the blackbody is in many ways essential to the understanding of quantum photonic devices, and LEDs in particular. Since we have developed the subject from a historical perspective, this has led us to mention several renowned scientists, including Nobel Prize laureates from the 20<sup>th</sup> century. It is therefore logical that we conclude this paper by recalling that 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.” The Nobel committee was not mistaken: LED technology has a bright future ahead of it!

## Appendix: Planck’s steps to the discovery of quantum theory

Planck wanted to interpret Eq. 10 which he had discovered empirically. His original derivation of that equation made him the discoverer of quantum theory [21]. To appreciate the importance of his work, we shall outline the three steps he took.

### 1. Classical electromagnetic theory

First, he established the relation:

$$u_\nu(\nu, T) = \frac{8\pi\nu^2}{c^3} U_\nu(\nu, T) \quad \text{Eq. 45}$$

between the energy density  $u_\nu$  of the equilibrium radiation at temperature  $T$  and the average energy  $U_\nu$  of a resonator of frequency  $\nu$  and temperature  $T$ . He completed this proof on the basis of classical electromagnetic theory. Comparing Eq. 10 and Eq. 45, he could then find  $U_\nu$ :

$$U_\nu(\nu, T) = \frac{h\nu}{e^{k_B T} - 1} \quad \text{Eq. 46}$$

### 2. Thermodynamics and entropy

Planck was a convinced promoter of entropy. In the second step, he determined the entropy,  $S$ , of the resonators by integration of  $TdS = dU$ . From Eq. 46, he evaluated  $T$  as a function of  $U_\nu$  for a fixed frequency  $\nu$ . He obtained:

$$S = k_B \left[ \left(1 + \frac{U_\nu}{h\nu}\right) \ln \left(1 + \frac{U_\nu}{h\nu}\right) - \frac{U_\nu}{h\nu} \ln \frac{U_\nu}{h\nu} \right] \quad \text{Eq. 47}$$

### 3. Statistical thermodynamics

The third step was the revolutionary one. To complete this ultimate stage, he drew heavily on Boltzmann’s work on statistics and entropy [22], [23]. To this end, he considered a system of  $N$  resonators vibrating at frequency  $\nu$ . The total energy of these oscillators is  $U_N = N U_\nu$ , to which corresponds a total entropy  $S_N = N S$ . In an “act of desperation”, as he would qualify it later, he then made the *ad hoc* assumption that the total energy was made up of finite energy elements  $\varepsilon$ , such that  $U_N = P \varepsilon$ , with  $P$  a large integer.

He followed one of Boltzmann’s ideas according to whom entropy, apart from an additive constant, is proportional to the logarithm of the number  $W$  of “complexions” that constitute the equilibrium state of the system. Although Boltzmann never wrote down the equation, Planck formulated it as follows:

$$S_N = k_B \ln(W) + \text{const.} \quad \text{Eq. 48}$$

Then, he calculated the number  $W$  of “complexions” (or permutations in combinatorics)<sup>6</sup> for a discrete system consisting of  $P$  energy elements that are distributed between  $N$  resonators:

$$W = \frac{(N + P - 1)!}{(N - 1)! P!} \quad \text{Eq. 49}$$

Applying Stirling’s formula,<sup>7</sup> he found:

$$W \approx \frac{(N + P)^{N+P}}{N^N P^P} \quad \text{Eq. 50}$$

<sup>6</sup> Planck chose the symbol  $W$ , which is the first letter of “Wahrscheinlichkeit”, the German word for probability.

<sup>7</sup>  $\ln(N!) = N \ln(N) - N$

Finally, using  $P/N = U_v/\varepsilon$  and  $S = S_N/N$ , he obtained:

$$S = k_B \left[ \left(1 + \frac{U_v}{\varepsilon}\right) \ln \left(1 + \frac{U_v}{\varepsilon}\right) - \frac{U_v}{\varepsilon} \ln \frac{U_v}{\varepsilon} \right] \quad \text{Eq. 51}$$

Since entropy only depends on  $U_v/\varepsilon$  according to Wien's displacement law, it follows from the comparison of Eq. 47 and Eq. 51 that

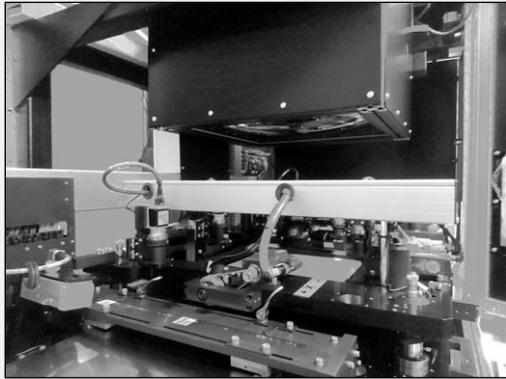
$$\varepsilon = h\nu \quad \text{Eq. 52}$$

This is how quantum theory was born. Planck has been quite criticized for his audacity on this third step, especially for his use of Eq. 49 for which he had no justification, except that it was giving him the result he was looking for...

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