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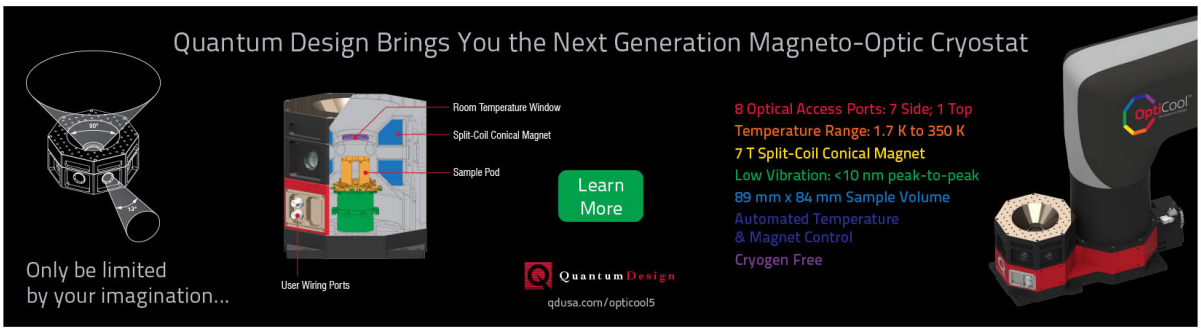

Temperature invariant energy value in LED spectra

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Relative emission spectra of light-emitting diodes (LEDs) depend on the junction temperature. The high-energy region of the emission spectrum can be modelled with Maxwell-Boltzmann distribution as a function of energy and junction temperature. We show that according to the model and our experiments, the normalized emission spectra at different junction temperatures intersect at a unique energy value. The invariant intersection energy exists for many types of LEDs and can be used to determine the alloy composition of the material. Furthermore, the wavelength determined by the intersection energy can be used as a temperature invariant wavelength reference in spectral measurements. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4971831]

Semiconductor alloys from the element groups III and V are the most important materials for fabricating visible light-emitting diodes (LEDs).[1] In addition to lighting and indication applications, LEDs are widely used in spectroscopy or in scientific applications such as a spectrally adjustable radiance sources.[2–4] An LED emits a quasi-monochromatic spectrum, but the characteristics of an LED, such as the peak wavelength, intensity, bandwidth, and forward voltage vary as a function of temperature and between LED specimens, even of the same type.[5] To use LEDs for accurate measurements, precise calibration of their optical and electrical characteristics is required.[6–8]

The emission spectrum of an LED is generated by electron-hole recombination and can be modelled as a product of the joint density of states of electrons and holes and the Maxwell-Boltzmann distribution.[1,5] The intensity and the peak wavelength of light emitted by an LED depend on the junction temperature of the LED. Thus, when using LEDs in metrological applications or as calibration sources, the junction temperature of the device needs to be stabilized.

In this Letter, we show that the relative LED spectrum, normalized to the peak intensity, has an energy value E_B, where the relative intensity is constant, i.e., independent on the junction temperature. This energy can be used as an invariant parameter for the measured LED. On the basis of these findings, we derive a method to determine the band gap energies of LEDs manufactured using semiconductor materials from the element groups III and V. The method is based on measuring LED spectra at varied, but unknown, junction temperatures, and the method is applied to determine the alloy composition of III–V semiconductors. As another type of application, it is concluded that the method provides practical wavelength references for spectroradiometer calibrations.

A blue and a red LED were characterized for their spectra at varied temperatures. The blue LED was manufactured by Aalto University, and the semiconductor layer structure is known in detail. The red LED was a Thinfilm InGaAlP device from Osram Opto Semiconductors, and the layer composition is not known in detail.[9]

The blue LED structure consisted of a sapphire wafer, a Si-doped n-GaN layer, a single InGaN/GaN quantum well, and a magnesium doped p-GaN layer.[10] Ti/Al/Au metal scheme was used for n- and p-metal contacts. The processed wafer was polished and diced into individual LED chips and then bonded onto silver-coated TO (transistor outline) headers to perform the measurements.[11] Details of the LED growth process can be found in Ref. 12.

The LEDs were attached to a temperature controlled heat sink, and the junction temperature was varied by changing the temperature of the heat sink.[13] Spectral measurements were carried out using a calibrated Konica Minolta CS2000 array spectroradiometer, and the obtained spectra were normalized to the maximum value. The intensity calibration of the spectroradiometer was carried out using a calibrated FEL lamp, which is traceable to the spectral irradiance scale of the National Standards Laboratory of Finland.[14] The wavelength scale of the spectroradiometer was calibrated against spectral lines of a mercury argon calibration source.

Figure 1 shows the normalized spectra of the blue and red LEDs measured at different temperatures. For the blue LED, the temperatures of the p-n junction were not known but the temperatures of the TO-base were used. For the red LED, the junction temperature dependence on the forward voltage was characterized, and the absolute junction temperatures were used.[5]

The intersection points in Figure 1 are located at energies $E_B = (2.837 \pm 0.003)$ eV and $E_B = (2.141 \pm 0.002)$ eV for the blue and red LEDs, respectively, at 95% confidence level. The corresponding relative intensities for the intersection points were 39% and 0.77% of the peak intensity. The Konica Minolta CS2000 spectroradiometer used for the measurement had a spectral resolution of 1 nm corresponding to 0.0065 eV at 2.837 eV and 0.0036 eV at 2.141 eV. Due to the limited resolution, the spectra were interpolated, and the intersection point between each individual pair of curves was determined. The intersection energies stated were calculated

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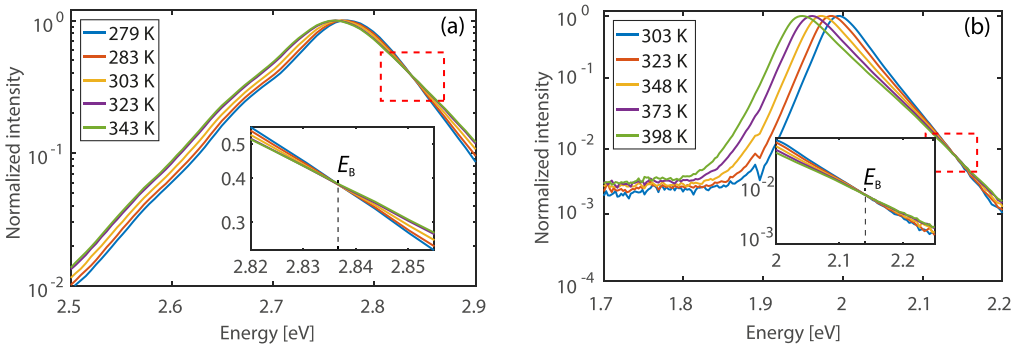

FIG. 1. Normalized spectra of the blue (a) and red (b) LEDs, and the close ups of the intersection energies E_B, measured at different temperatures. In (a), the figure legend gives heat sink temperatures. In (b), the figure legend gives junction temperatures.

as an average of the values obtained. The standard deviations for the intersection points were 0.0015 eV and 0.0009 eV for the blue and red LEDs, respectively.

The intersection energy in Figure 1 can be derived from the well-known model for LED emission spectra at different temperatures. An LED emits light as a result of spontaneous recombination of electron-hole pairs. The emission spectrum of an LED has been mathematically modelled earlier by numerous researchers.[1,15,16] The emission intensity of an LED is proportional to the product of the joint density of states f and the exponential Boltzmann distribution of carriers

$$I(E,T) \propto f\big(E - E_g(T)\big) \times e^{-\frac{E-E_g(T)}{kT}}, \tag{1}$$

where E is the photon energy, $E_g(T)$ is the band gap energy at junction temperature T, and k is the Boltzmann constant. Most of the present high power LEDs are based on quantum-well structure, where the motions of electrons and holes are confined in two-dimensional wells. In quantum well LEDs, the densities of states of the carriers are theoretically derived to be step functions. However, the measured joint density of states follows a broadened, rounded step function[16] with an unknown detailed shape. For LEDs manufactured using bulk, direct band gap semiconductors, the theoretical joint density of states follows the square root $[E - E_g(T)]^{1/2}$,[16] but here we allow any energy dependence for the density of states $f(E - E_g(T))$.

As can be seen from the measurement results in Figure 1, the intensity of the normalized spectra at the energy E_B does not depend on temperature

$$\frac{I(E_B,T)}{I\big(E_{max}(T),T\big)} = \frac{f\big(E_B - E_g(T)\big)}{f\big(E_{max}(T) - E_g(T)\big)} \times e^{-\frac{E_B - E_{max}(T)}{kT}}, \tag{2}$$

where $E_{max}(T)$ is the energy at the peak of the spectrum. All exponential energy dependencies are collected in the Boltzmann factor. Thus the exponent in Eq. (2) must be independent of temperature, which implies that

$$E_{max}(T) = E_B - qkT, \tag{3}$$

where q is a positive constant defining the shift of the peak energy of an LED spectrum as a function of temperature. Values of q determined from Figs. 1(a) and 1(b) are 2.56 and 5.57, respectively.

An LED spectrum shows a redshift in the peak energy with increased junction temperature due to the reduced bandgap with an increasing temperature.[17] The temperature dependent bandgap energy $E_g(T)$ in Eqs. (1) and (2) can be expressed as a linear approximation when $T \gg 0$ K.[18] Since the temperature range during our measurements was between 279 K and 398 K, the linearized band gap energy can be approximated as

$$E_g(T) = E_0 - pkT, \tag{4}$$

where E_0 represents the linearly extrapolated band-gap energy at 0 K, and p is a positive constant defining the band gap shift of an LED as a function of temperature.

The energy $E_{max}(T)$ at a maximum intensity of Eq. (1) can be found from the zero of the derivative

$$\left.\frac{\partial I(E,T)}{\partial E}\right|_{E=E_{max}(T)} = 0. \tag{5}$$

This leads to a differential equation

$$kT\frac{f'\big(E_{max}(T) - E_g(T)\big)}{f\big(E_{max}(T) - E_g(T)\big)} = 1. \tag{6}$$

Equation (6) can be solved using Eqs. (3) and (4) and substituting $T = (\varepsilon - E_B + E_0)/(k(p-q))$, where ε is a new energy variable. The solution of the obtained first order differential equation with variable ε is

$$f(\varepsilon) = r(\varepsilon - E_B + E_0)^{p-q}, \tag{7}$$

where r is an integration constant. Substituting the temperature dependent band gap energy as in Eq. (4), we get

$$f(E - E_g(T)) = r(E - (E_B - pkT))^{p-q}. \tag{8}$$

From Eqs. (8) and (4), we can conclude that $E_B = E_0$, which means that the intersection energy E_B is the linear extrapolation of the band gap energy from room temperature to 0 K.

From Eq. (2), using the solution (8) for the density of states, we can conclude that at the photon energy E_B, the relative intensity does not depend on temperature

$$\frac{I(E_B,T)}{I(E_{max},T)} = \left(\frac{p}{p-q}\right)^{p-q} e^{-q}. \tag{9}$$

The obtained invariant energy value E_B is a general feature of all LEDs over the temperature range where the linearizations described by Eqs. (3) and (4) apply. We have observed the invariant crossing point for a large number of different types of LEDs, including white LEDs and infrared LEDs. Different LED architectures can have an effect on parameter q in Eq. (3), which has the main influence on the relative intensity of the invariant point via Eq. (9). The values of p solved from Eq. (9) are 4.40 and 5.78 for the blue and red LEDs of Fig. 1, respectively. In contrast to parameters p and q, determination of E_B does not require absolute junction temperatures or known temperature differences, but it is sufficient to vary the junction temperature, observe changes in the spectra, and to determine the invariant crossing point in the relative spectra.

Figure 2 shows the measured and modelled spectra of a GaAs infrared LED and the close up of the temperature invariant intersection point. Measured LED spectra in Figures 1 and 2 tend to be more symmetrical than Eqs. (1) and (8) predict. The real spectra of quantum-well LEDs do not rise sharply as the stepwise joint density of states predicts, but the spectra are broadened.[16] The difference between the model and the measured spectrum is due to subbandgap recombination which affects the low-energy side of the spectrum.[5] Equation (1) is thus valid only on the high-energy side of the spectrum.[19] For detailed analysis, it should be noted that it is possible to add on the right-hand-side of Eq. (1) any function of $E - E_g(T)$, which has zeros at $E = E_{max}(T)$ and $E = E_B$ and a zero slope at $E = E_{max}(T)$. Equations (2), (5), and (9) then remain unchanged, still proving the existence of the temperature invariant energy value.

In Eq. (4), the temperature dependence of the band gap energy is linearized for temperatures $T \gg 0$ K. Previous studies[1,18] have shown that the temperature dependence of the band gap energy follows the second order Varshni equation at temperatures $T < 290$ K.[20] The difference between the band gap energy at 0 K, predicted by the second order Varshni equation, and the measured energy E_B for a typical GaN LED is less than 2%, when using band parameters from the literature.[21] According to our studies and the results by Keppens *et al.*,[18] other compound semiconductor materials show similarly small differences between $E_g(0)$ and E_B.

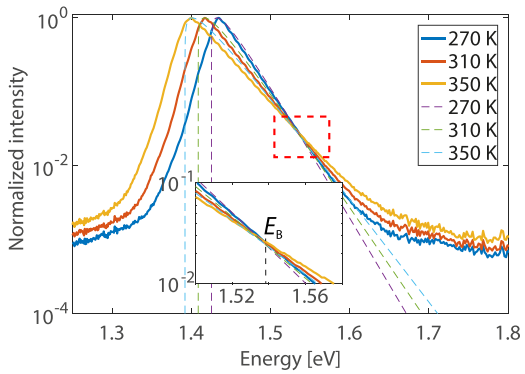

FIG. 2. Normalized (solid lines) and modelled (dashed lines) spectra of a GaAs LED at different temperatures, demonstrating the temperature invariant energy value E_B for an LED operating at infrared wavelengths. As explained in the text, there are large deviations at the low-energy side and a perfect fit by Eqs. (1) and (8) is not expected even between the peak energy value and the crossing point. For the dashed lines, the parameter values are $p = 4.85$ and $q = 4.55$.

The blue InGaN/GaN LEDs manufactured by Aalto University were grown using metalorganic vapour phase epitaxy reactor,[10] and the alloy decomposition of the LEDs was known to be approximately $In_{0.15}Ga_{0.85}N$. For the $In_xGa_{1-x}N$ alloy, the composition dependent band gap at $T = 0$ K is given by[1]

$$E_g(x) = xE_{g,InN} + (1-x)E_{g,GaN} - bx(1-x), \qquad (10)$$

where $E_{g,InN} = 1.994$ eV and $E_{g,GaN} = 3.507$ eV are the band gaps for bulk InN and GaN at 0 K, and $b = 3.0$ eV is the band gap bowing parameter for $In_xGa_{1-x}N$.[21]

For the studied blue InGaN/GaN LED, the temperature invariant point E_B was found to be 2.837 eV as seen in Figure 1(a). This corresponds to the linear extrapolation of the band gap from the room temperature to 0 K as stated in Eq. (4). In order to be able to substitute E_B to the left-hand-side of Eq. (10), the second order Varshni equations describing the temperature dependent band gaps $E_{g,InN}(T)$ and $E_{g,GaN}(T)$ were also linearized at the operating point of 311 K and then extrapolated to $E_{B,InN} = 2.011$ eV and $E_{B,GaN} = 3.563$ eV at 0 K. The operating point of 311 K was selected as the average temperature of the spectral measurements. Solving x from Eq. (10), we can find that $x = 0.18$, which agrees with the indicatively known alloy content of $x = 0.15$. The standard deviation of 0.0015 eV in E_B leads to 1.1% deviation in the alloy content. Due to the inaccuracies in the experimental band gap parameters, especially in the case of InN, where the literature values for the band gap vary between 0.7 eV and 3.1 eV,[21,22] and due to the linearization, we estimate the relative standard uncertainty of the method to be 10% in x.

As another application, we consider to use the invariant energy value E_B as a spectrometer calibration reference. The usual way of checking the wavelength scale of a spectroradiometer is to measure the spectrum of a line source with a known emission wavelength, such as a mercury lamp or a laser. Due to the temperature dependence of the band gap energy, LEDs are not suitable for calibration purposes without a precision temperature control.

Based on the model and measurement results shown above, an LED can be characterized for a temperature independent energy E_B. Using multiple characterized LEDs in a tight package, the E_B energy values of the individual LEDs can be used as reference wavelengths to calibrate the wavelength scale of a spectroradiometer. As compared to temperature stabilized LED references, our method does not require a high accuracy temperature stabilizer, only a possibility of operating at two different temperatures is required. According to our measurement results, E_B can be resolved with an accuracy that is two times better than the spectral resolution of the spectrometer used. Furthermore, the method also gives information on the intensity scale of the spectroradiometer: Any nonlinearity in the scale would distort the relative spectra in such a way that a unique intersection point E_B would not be observed.

In conclusion, the spectra as a function of junction temperature of an LED were modelled and measured for three different types of LEDs manufactured using III–V semiconductor

materials and a method to characterize the band gap energy of an LED was developed. The method can be applied to determination of the alloy composition of the LED semiconductor layers and as a wavelength reference for a spectroradiometer. Preliminary measurements were also carried out for a white LED with luminophore and for a double junction III–V solar cell. It was possible to determine the intersection energies E_B and alloy compositions for these samples as well.

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