Development of Cd-free QD-LEDs for Display Applications and Improvement of Luminous Efficiency

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ABSTRACT

We discuss development of QD-LEDs using Cd-free quantum dots (QDs) which emit by current injection. This technology is expected to be a key of next-generation display with wide color gamut and high energy efficiency. Designs that take current injection efficiency and carrier balance into consideration, along with the quantum efficiency of the QD itself, are effective in improving the characteristics. In addition to confirming the expansion of the color gamut by reducing the FWHM of the QD material, we have achieved patterning in a size practical for highresolution displays, estimating the expected EQE derived from the optical evaluation of QDs and the equivalent circuit model of QD-LEDs, and directly measuring the carrier injection efficiency based on photoelectrochemical measurement.

1 Introduction

QD-LEDs, which emit lights by injecting current into quantum dots, are a promising technology for nextgeneration displays that combines high color purity and luminous efficiency, as the emission wavelength can be tuned by the size of the QDs. The high color purity enables high-contrast luminescence without color filters.

As is well known, the luminescence properties of quantum dots are caused by the discretization of energy due to the electron confinement effect (quantum effect), and for particle sizes below the Bohr radius, the emission wavelength varies depending on the particle size. Energy calculations based on the effective mass approximation are in good agreement with measured emission wavelengths. QD applied laser diode has already been developed as an application for current injection into quantum dots [1].

The product images of such QD-LED displays are also expected to be used for indoor and outdoor signage applications, taking advantage of their low energy consumption, high resolution, and thinness of panel. The advantage of QD-LEDs for high-definition displays include high luminance efficiency due to self-luminescence with high color purity, adaptability to photolithography, high resolution and large light-emitting area with top emission structure, and high reliability. The high transmittance without color filters is particularly attractive from the viewpoint of high color gamut and low energy consumption.

To achieve these goals, it is important to develop quantum dot materials, ambient structures that achieve high current injection efficiency, and photolithography technique. In developing quantum dot materials, optimum wavelength control by particle size tuning, and realization of steep emission peak with narrow half value width are necessary. In the current injection efficiency, establishment of carrier balance of electrons and holes, and improvement of carrier injection into QDs are essential. In the photolithography, both large size and high resolution, as well as the separation of QDs consisting of RGB are the major issues.

2 Experimental results

Development of high luminous efficiency and high stability QD-LEDs using Cd-free QD materials are still halfway, mainly because choices of Cd-free materials that can emit visible light are limited. Especially, blue QD materials compatible with narrow linewidth and high efficiency are still in the development stage.



Fig. 1 (a) PL spectrum of Cd-free blue QD (b) Color gamut of developed QD-LED

Figure 1(a) shows the emission spectrum of blue Cdfree QDs developed with narrow FWHM of less than 20 nm. As shown in Figure 1(b), the color gamut of 106% relative to the BT2020 standard in terms of area ratio has been achieved [2].



Fig. 2 Electroluminescence image of RGB Cd-free QD-LED

Figure 2 shows the electro-luminescence image of a QD-LED device formed in a pixel pattern shape using Cd-free RGB QDs. The pixel pattern size is applicable to high-definition displays using photolithography, and the basic electrical properties for display applications have been confirmed.

3 Approaches to luminance improvement

In analyzing QD-LEDs, it is effective to introduce indices that can evaluate both optical and current injection characteristics. Designing device structures and materials based on these indices lead to improvement.

As shown in Equation 1, the external quantum efficiency (*EQE*) is expressed as the product of the internal quantum efficiency (*PLQY(film)*), the carrier injection efficiency ($\eta_{injection}$), and the light extraction efficiency ($\eta_{extraction}$), of which the carrier injection efficiency is obtained from the carrier balance factor between electron and hole and exciton generation probability.

$$EQE = PLQY(film) \times \eta_{injection} \times \eta_{extraction}$$
(1)

In order to improve the efficiency of QD-LEDs, it is necessary to control (1) the efficiency of QDs, (2) the luminous efficiency of the device, (3) the current contributing to luminescence, and (4) the carrier balance. In the QD-LEDs, as the QDs are formed as thin films, the PL fluorescence lifetime measurement is useful to derive the photoluminescence quantum yield (*PLQY(sol*)) of the solution versus that of the thin film (*PLQY(film*)), which can be accurately derived from the ratio between the emission lifetime $\tau_{PL,sol}$ in solution and $\tau_{PL,film}$ in thin film as shown in Equation 2.

$$PLQY(film) = PLQY(sol) \times \frac{1/\tau_{PL,sol}}{1/\tau_{PL,film}}$$
(2)

Figure 3 shows an example of the relationship between optically determined EQE and measured EQE using the derived quantum yields of thin films. Here, the optically obtained EQE is defined as 100% for the carrier injection efficiency ($\eta_{injection}$) and 20% for the light extraction efficiency ($\eta_{extraction}$) in Equation 1.

As can be seen in Figure 3, there are some cases where the optically determined EQE and the measured EQE are in good agreement, while there are others where the measured EQE is smaller.

To interpret this, the diode coefficient *n* was derived by component-decomposing the current flowing in the device from the voltage-current curve based on the equivalent circuit model of the QD-LED shown in Figure 4. Applying this to the results in Figure 3, it is clear that the optically determined EQE and the measured EQE are almost identical for devices with a value close to n=2(the ideal value of the recombination diode contributing to light emission,) and that the difference between each other increases as the diode factor becomes larger.



Fig. 3 Measured and optically estimated EQEs with diode coefficients



Fig. 4 Equivalent circuit of QD-LED

In addition to such device evaluation, injection efficiency evaluation using photoelectrochemical measurement method as shown in Figure 5 is effective to discuss carrier injection into QDs [3-5]. The advantages of using this method include: (1) evaluation with simple configuration of QDs on the electrode film, and (2) direct evaluation of carriers generated in the QDs. The correlation between shell thicknesses measured in this way and photocurrents have been observed. This method is especially effective in deriving the optimal shell thickness of QDs.



Fig. 5 Photoelectrochemical measurement of QDs

4 Conclusions

In the development of QD-LEDs for high-definition displays, we confirmed a wide color gamut by applying Cd-free QDs and EL emission for RGB at a practical pixel size.

In order to improve the characteristics of currentinjection light-emitting devices using quantum dots, evaluation of optical property, as well as the carrier balance between electrons and holes, and the carrier injection efficiency into the QDs play important roles. Time-resolved PL analysis with equivalent circuit model, and photoelectrochemical measurement enable integrated analyses and provide effective guidelines for improving luminous efficiency of QD-LEDs.

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