Development of Efficient Blue Cadmium-Free Quantum Dot Light-Emitting Diodes

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ABSTRACT

This paper reports the efficient blue cadmium-free quantum dot light-emitting diodes (QD-LED). The blue cadmium-free QD-LED with well optimized structure exhibits high EQE. These new QDs have great potential to be used in next generation QD-LED display with wide colour gamut.

1 INTRODUCTION

Quantum dots (QDs) are very excellent materials for displays because of their outstanding properties. QDs can emit all visible light from blue to red colors by changing their size within several nanometers. QDs have adjustable emission, high quantum yields and narrow emission linewidth which are realized from their quantum effect. Their optical properties are therefore promising for next generation displays to provide high luminance and wide color gamut.

Presently, QDs are being used in two configurations in displays. The first is a color conversion film (QD film) where QDs embedded into a matrix as using their photoluminescence property. These are used to convert blue light from backlight into red and green light in a liquid crystal display. The second is using QDs as light emitters into a light emitting diode based on electroluminescence (QD-LED). This is more efficient in principle than using QDs as light converters. Both QD film and QD-LED display can show a considerable expansion of color gamut, as required for new generation displays offering performance closer to the BT2020 standard.

QD-LED has been expected to show higher potential than any other QD photoluminescence-based displays to meet optimal performances. Recently Cadmium-based red-, green-, and blue-emitting QD-LEDs have shown the best performances critical to determine suitability for display application[1,2]: external quantum efficiency (EQE), chromaticity relative to display standard primaries, and operating lifetimes.

The most important factor to realize the next-generation displays is to achieve high-efficient blue emitting QD-LEDs. In order to meet the BT 2020 color gamut, blue emission wavelength should be longer than 450nm. EQE close to 20% has been demonstrated at wavelength over 460nm for Cd based QD-LEDs [3]. ZnSe based materials has been reported as blue emitting Cd-free materials[4, 5]. The highest efficiency reported for Cd-free based QD-LEDs, where ZnSeTe was used as Cd-free QD, was at 453nm. For ZnSe QDs, it is in theory possible to achieve emission at longer wavelength by increasing their sizes. However this also comes with degradation of the crystal quality and generation of non- radiative defects. On the other hand, for ZnSeTe QDs, it creates difficulty in controlling a precise alloy composition resulting in wider emission linewidth. Also ZeSeTe show low reliability which might arise from their alloy composition. Furthermore another possibilities are Indium Phosphide based materials[6]. These materials can show good optical properties except for emission line width.

Table 1 summarizes the light emission properties of the most efficient blue emitting QD-LEDs reported to date [3,4,5,6].

Table 1. Blue QD-LEDs reported in the literature

Material	λ (nm)	FWHM (nm)	Max. EQE	Ref. No.
CdSe	468	20	19.8	3
ZnSe	429	16	7.8	4
ZnSeTe	453	29	11.5	5
InGaP	465	45	2.5	6

2 EXPERIMENT

2.1 Blue Cd-free QD

We have developed ZnSe QD emitting at longer wavelength with high efficiency by using zinc sulfide (ZnS) as shell material. And We also developed a modified synthesis procedure of (ZnSe/ZnS) core/shell QD structure for optimization of blue Cd-free QD-LED.

2.2 QD-LED fabrication

QD-LEDs were fabricated with a basic bottom emitting structure as shown in Figure 1. All the layers were deposited by spin coating except for the cathode layer, which was thermally evaporated.

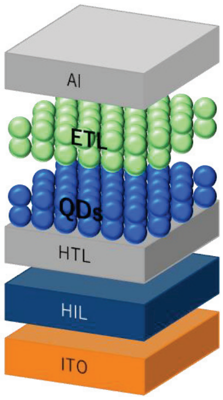

Figure 1. Schematic image of bottom emitting structure.

2.3 Optimization of band alignment

Figure 2 exhibits the energy band diagram of blue QD-LED with ITO / PEDOT:PSS / PVK / QDs / ETL / Al. The Zinc oxide nanoparticle solutions were spin-coated onto the QD layer as ETL layer, and the several variation of Zinc oxide solutions were synthesized through sol-gel process. In general adjusting the energy level of the electron transport layer, the electron injection efficiency into the light emitting layer can be controlled. The energy band level of the Zinc oxide is controlled by changing the synthesis precursors and conditions.

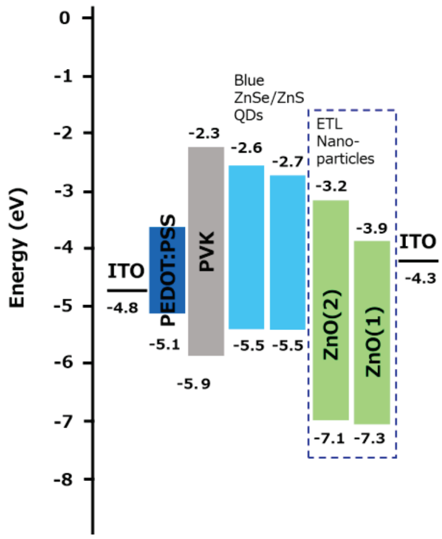

Figure 2. Energy band diagram of the Blue QD-LED studied in this work

3 RESULTS

3.1 Device performance

Figure 3 shows electroluminescence (EL) of QD-LED fabricated using our ZnSe/ZnS QDs. This QD-LED has brilliant blue emission with using ZnSe QDs. The ZnSe QDs emit efficiently because of good current injection.

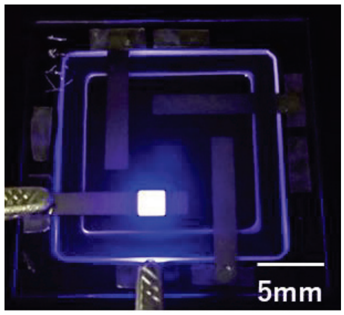

Figure 3. EL image of Blue Cd-free QD-LED under an applied voltage of 5 V.

Figures 4 and 5 show EL spectrum and EQE curve as a function of current density. Max efficiency is 10.7% and the emission wavelength is 445nm with a FWHM of 15 nm. Electron and hole transport layers were optimized for balance of career concentration. By using our optimized ETL materials, the high EQE achieved indicate a good carrier injection. And their emission spectrum have quite sharp. The emission linewidth of these ZnSe are smaller than Cadmium type QDs. It is due to their crystallinity and well controlled size dispersion.

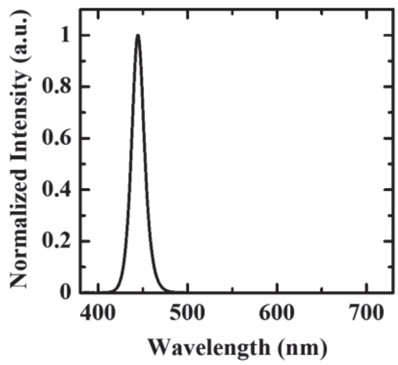

Figure 4. (a)EL spectrum of blue Cadmium-free QD-LED.

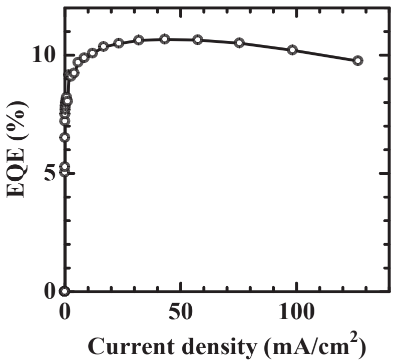

Figure 5. EQE as a function of current density of blue Cadmium-free QD-LED.

3.2 Comparison of performance by changing ETL

We try to optimize the carrier valance of the blue QD-LED. Blue emitting QDs generally have shallow energy level of conduction band. So we focus on the optimization of energy band diagram of ETL materials. We synthesized several varieties of Zinc oxide-based nanoparticles. QD-LED fabricated with ZnO(2) shows EQE=10.7%. It is higher than using ZnO(1). The carrier valance of QD-LED with ZnO(2) should be much better than ZnO(1). Probably It is thought that electron injection became well because of shallow energy level of ZnO(2).

4 CONCLUSIONS

We have reported high efficient blue Cd-free QD-LED. We succeeded in synthetization of blue ZnSe/ZnS QDs having high PLQY with FWHM less than 15 nm. By carefully controlling QD-LED structures, ZnSe QD emitting at 445nm have been demonstrated with high EQE 10.7%. These results are very encouraging for the use of ZnSe as blue emitters in QD-LED display.

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