Efficient Top Emission Light-Emitting Diode Based on Cadmium-Free Quantum Dots

Shuaibing Li[1]*, Dong Li[1]*, Zhuo Chen[1]*, Yanzhao Li[1]*
1 BOE Technology Group Co., Ltd., Beijing, 100176, P.R.China
***lishuaibing@boe.com.cn**

Abstract

Quantum Dot Light-Emitting Diodes (QLEDs) have attracted widespread concern from both academia and industry due to their advantages on high color gamut and resolution. In recent years, one of the main difficulties for QLED display technology is to replace cadmium based quantum dots, which have high toxicity. Indium phosphide (InP) and zinc selenide (ZnSe) materials are counted as the most promising alternative ones for red-green-blue quantum dots, respectively. In this paper, we simulated the frontal emission of top emission (TE) QLED devices and verified the implications of each functional layer thickness for emission spectrum of QLEDs. Finally, by adjusting the structure of QLED devices at electrical and optical aspects, we obtained TE QLED devices with distinguished light extraction efficiency and carrier injection balance, exhibiting higher current efficiency and narrower full width at half maximum.

Author Keywords

Cadmium-free quantum dots; QLEDs; Top emission; Angular distribution

1. Introduction

Today, consumer demand for display products is focused on high image clarity, low power consumption, and compatibility with intelligent systems. To meet these needs, display products need high resolution, wide color gamut, and high efficiency. In various display technologies, such as organic light-emitting diodes (OLEDs) [1, 2], Micro-LED [3, 4], laser displays [5], and quantum dot light-emitting diodes (QLEDs) [6, 7], many technologies have been significantly improved to meet market requirements.

After the first report in 1994 [8], the performance of QLED has gradually improved, and external quantum efficiency (EQE) has reached 20% [9, 10], which is comparable to that of commercial OLEDs and close to the theoretical limit [11]. However, in the reported QLED devices, most of them contain heavy metal elements, which are highly toxic to environment, so it is critical to find materials that are free of heavy metals. Based on this, cadmium-free quantum dots materials have aroused people's interest, and cadmium-free QLEDs have become an important direction for the development of QLEDs technology in the future. Among cadmium-free materials, II-VI ZnSe-based, III-V InP-based luminous materials with environmentally friendly properties achieved high-performance, and their QLED devices have made great progress [12]. However, due to the limitation of InP quantum dot materials, half-height width (FWMH) of InP QLED devices is almost above 40 nm, which is harmful for achieving wide color gamut. On the other hand, the QLED devices reported in the literature mostly adopt bottom emission structure, which will limit the opening ratio of display panel to a very low level, final limiting panel resolution. In QLED devices, (TE) structure can be controlled by optical microcavities to improve panel resolution. Therefore, in order to achieve high resolution, TE device structure is the inevitable choice.

In this paper, we have prepared cadmium-free QLED devices based on TE structure. For red, green and blue QLED devices, the maximum current efficiency can reach 24/69/11.8 cd/A by optimizing the electrical balance and front light output efficiency of QLED devices. At the same time, based on the micro-cavity control of TE structure, the FWMH of QLED devices are significantly improved, which provides us with another effective way to improve the color gamut of QLED in addition to material optimization.

2. Results and discussion

2.1. Device structure design

Cadmium-free QLED devices adopt organic-inorganic hybrid structure, and the structure diagram is shown in Figure 1. In the TE device, Ag and ITO were used as anode, which has strong reflective characteristics. The TE device structure is glass/Ag/ITO/HI/HT/QD/ET/Mg:Ag. Here, hole injection layer (HIL) is PEDOT: PSS. At the same time, due to the highest occupied molecular orbital (HOMO) energy level of QD layer is deeper, hole transport layer (HTL) typically need to match energy level of QD layer, where polymer [(9, 9-di-octylfluorenyl-2, 7-diyl)-Alt-(4,4'-(N-(4-N-butyl) phenyl)-diphenylamine) (TFB) was used as hole transport material with hole mobility of 10^{-2} cm^2/Vs and HOMO level of -5.3 eV. Furthermore, InP quantum dots was adopted as red-green light-emitting layer (EML) material, ZnSe quantum dots as blue EML material. Meanwhile, ZnMgO as electron transport layer (ETL) material. Furthermore, the thickness of top electrode Mg:Ag is 15 nm. Carriers were injected from ITO anode and Mg:Ag cathode, and then combined at quantum dot layer to realize electroluminescence (EL).

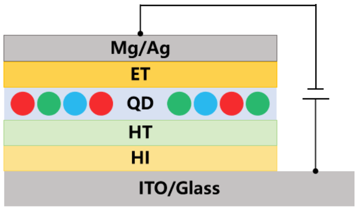

Figure 1. Structure diagram of QLED devices.

2.2. Optical structure optimization of cadmium-free QLED devices

For TE device structure, it is approximated as a Fabry-Perot cavity. In this case, emitting layer is located between Ag/ITO anode (bottom electrode) and thin Mg:Ag cathode (top electrode), where Ag/ITO electrode form a reflective mirror and Mg:Ag electrode is used as a translucent mirror. Before fabricating QLED devices, we first studied light extraction behavior of TE QLEDs based on various transport layer thicknesses. In this micro-cavity structure, there are generally two types of interference. As shown in Figure 2(a), directly emitted light and that reflected from bottom electrode, which has same wave vector with directly emitted light, can occur interference, and the interference is named as wide-angle interference; in Figure 2(b), the interference among multiple reflected light is called multi-beam interference.

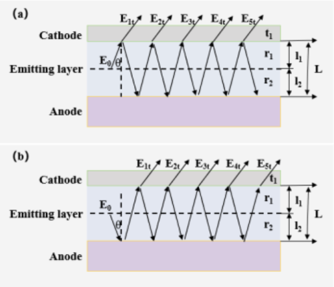

Figure 2. Fabry-Perot resonant cavity-schematic diagram of multi beam interference.

To achieve stronger front light output in TE QLED devices, we performed optical simulation of the above-mentioned device structure using SETFOS, a semi-conductor thin film optical simulation software, to optimize functional layer thickness. As shown in Figure 3, we can clearly see that the strong front emission of the TE device can only be achieved in relatively thinner HTL/ETL thickness range. The thickness of HT and ET in red TE device is about 30-40 nm and 25-35 nm, respectively. HT thickness and ET thickness in green TE device is about 20-30 nm and 25-35 nm, respectively. HT thickness in blue TE devices is about 35-45nm, and the thickness of ET is about 5-15nm. The simulation results show that the thickness of ET layer of red, green and blue devices is gradually thinner, and the thickness of ET layer for blue devices is the least.

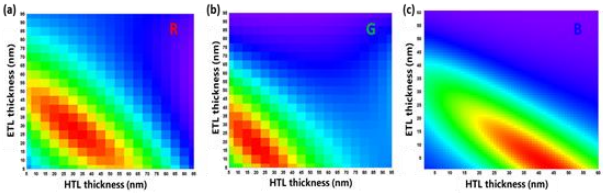

Figure 3. The relationship between the brightness of TE devices with HTL/ETL thickness based on SETFOS simulation: (a) R-QLED; (b) G-QLED；(c) B-QLED.

Figure.4 (a)-(c) shows the simulation results of angle distribution of EL emission under various ETL thickness, then the thickness range of ET layer was optimized again. As can be seen, in order to obtain a stronger front light output, the thickness of ETL in red and green TE device is among 40-50 nm and 25-35 nm, respectively. For blue TE device, the thickness of ETL is about 10-20 nm. This result is similar with that in Figure 3. Therefore, we can conclude that the thickness requirements of ETL for red-green-blue TE devices gradually become thinner. At this time, the light intensity of QLED devices at front direction is the strongest after thickness optimization, and the corresponding device efficiency should be the highest in theory. We simultaneously measured and summarized the angular distribution situation of red-green-blue TE devices under various ET thicknesses, which are shown in Figure.4 (d)-(f). These results are consistent with the above simulation results. This means that for different red-green-blue TE devices, required ET layer thickness needs to be successively reduced.

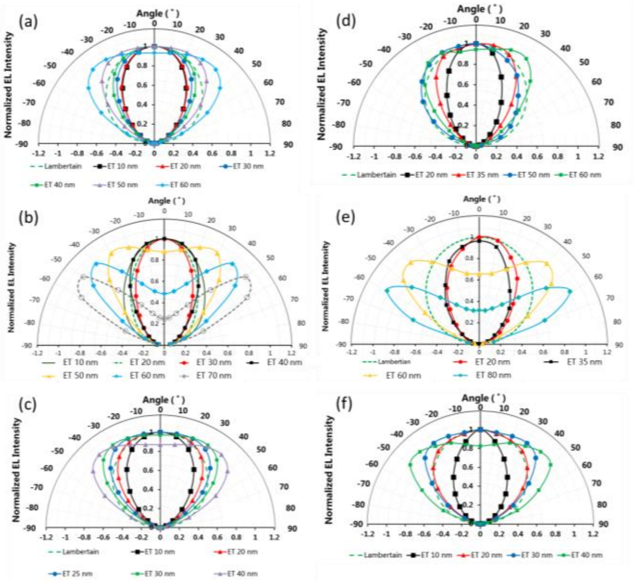

Figure 4. Simulation results of angle distribution of EL-intensity of TE QLED devices under various ET layer thicknesses: (a) R-QLED; (b) G-QLED; (c) B-QLED. Measurement results of angle distribution of EL intensity of TE QLED devices: (d) R-QLED;（e）G-QLED;（f）B-QLED.

As presented in Figure 5, we compared normalized EL spectra of the TE QLEDs. Compared with bottom emission QLEDs, the EL spectra of TE ones show a significant improved FWMH. The FWMH of red-green-blue TE QLED is reduced from 54nm/41nm/48nm to 37nm/31nm/43nm respectively, which is similar to those of CdSe-based devices. The above results indicate that profitable micro-cavity effect realized in current device structure. Due to only a specific emission spectrum distribution can meet resonance conditions, light ray is constantly reflected between the two electrodes. With adjusting cavity length, more excellent color purity can be obtained.

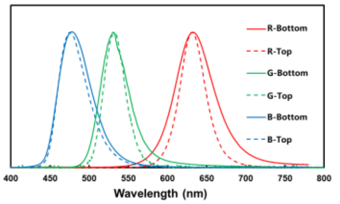

Figure 5. Normalized EL spectral of bottom and TE red-green-blue QLED devices.

The above results show that improved front light output efficiency and FWMH can be obtained , which indicate that TE device structure is conducive to realize high efficiency and high color gamut cadmium-free QLED.

2.3. Cadmium-free QLED devices

Based on the results of TE device structure optimization, we established the transport layer thickness. In terms of the optimization of QLED devices in electrical aspects, based on the existing functional layer materials, we selected an energy level system and screen suitable transfer/injection materials. Because quantum dots have a deep HOMO level, we compared different material systems in addition to the traditional PEDOT: PSS/TFB system, and chose the HIL-1/ HTL-2 system whose energy level is more compatible with that of quantum dots. Figure 6 shows the energy level diagram of above functional layers for this TE QLED with the HIL-1/ HTL-2 system.

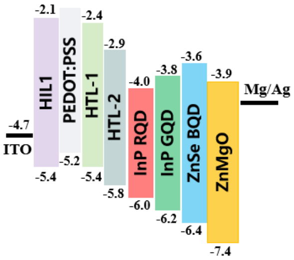

Figure 6. Schematic diagram of energy levels in various functional layers for TE QLED devices with HIL-1/HTL-2 system.

As shown in Table 1, the maximum current efficiency of red-green-blue cadmium-free devices reached 24 cd/A, 69 cd/A and 11.8 cd/A, respectively. This indicates that EL efficiency of cadmium-free QLED devices has been effectively raised through improved front light output.

Table 1 EL efficiency of TE red, green and blue QLED devices.

Devices	**EL efficiency (cd/A)**
R-QLED	24
G-QLED	69
B-QLED	11.8

3. Conclusions

In summary, this paper demonstrate high-efficiency TE red, green and blue cadmium-free TE QLED devices. From device engineering perspective, our TE cadmium-free QLED devices achieve higher efficiency and narrower FWMH than other cadmium-free QLED devices. By controlling optical micro-cavity, excellent device performance is obtained. In this paper, we completed the principle analysis and simulation of micro-resonator effect regulation of T QLED devices, and verified the implication of each functional layer thickness for device emission spectrum. We optimized the thickness of transport/quantum dot layers to achieve high front light extraction. The maximum current efficiency of red-green-blue cadmium-free TE QLED raised 24cd/A, 69cd/A and 11.8cd/A, respectively. We believe that our research can provide the necessary technical support for next generation of non-toxic QLED displays technology.

4. Reference

[1] Salehi, A.; Fu, X. Y.; Shin, D. H.; So, F. Recent advances in OLED optical design. Adv. Funct. Mater. 2019, 29, 1808803.

[2] Wei, Q.; Fei, N.; Islam, A.; Lei, T.; Hong, L.; Peng, R. X.; Fan, X.; Chen, L.; Gao, P. Q.; Ge, Z. Y. Small-molecule emitters with high quantum efficiency: Mechanisms, structures, and applications in OLED devices. Adv. Opt. Mater. 2018, 6, 1800512.

[3] Wu, T. Z.; Sher, C. W.; Lin, Y.; Lee, C. F.; Liang, S. J.; Lu, Y. J.; Chen, S. W. H.; Guo, W. J; Kuo, H. C.; Chen, Z. Mini-LED and Micro-LED: Promising candidates for the next generation display technology. Appl. Sci. 2018, 8, 1557.

[4] Huang, Y. G.; Tan, G. J; Gou, F. W; Li, M. C.; Lee, S. L.; Wu, S. T. Prospects and challenges of mini-LED and micro-LED displays. J. Soc. Inf. Disp. 2019, 27, 387–401.

[6] Rogach, A. L.; Gaponik, N.; Lupton, J. M.; Bertoni, C.; Gallardo, D. E.; Dunn, S.; Pira, N. L.; Paderi, M.; Repetto, P.; Romanov, S. G. et al. Light-emitting diodes with semiconductor nanocrystals. Angew. Chem., Int. Ed. 2008, 47, 6538–6549.

[7] Pietryga, J. M.; Park, Y. S.; Lim, J.; Fidler, A. F.; Bae, W. K.; Brovelli, S.; Klimov, V. I. Spectroscopic and device aspects of nanocrystal quantum dots. Chem. Rev. 2016, 116, 10513–10622.

[8] Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer. Nature 1994, 370, 354–357.

[9] Dai, X. L.; Zhang, Z. X.; Jin, Y. Z.; Niu, Y.; Cao, H. J.; Liang, X. Y.; Chen, L. W.; Wang, J. P.; Peng, X. G. Solution-processed, highperformance light-emitting diodes based on quantum dots. Nature 2014, 515, 96–99.

[10] Mashford, B. S.; Stevenson, M.; Popovic, Z.; Hamilton, C.; Zhou, Z. Q.; Breen, C.; Steckel, J.; Bulovic, V.; Bawendi, M.; Coe-Sullivan, S. et al. High-efficiency quantum-dot light-emitting devices with enhanced charge injection. Nat. Photonics 2013, 7, 407–412.

[11] Rhee, S.; Chang, J. H.; Hahm, D.; Jeong, B. G.; Kim, J.; Lee, H.; Lim, J.; Hwang, E.; Kwak, J.; Bae, W. K. Tailoring the Electronic Landscape of Quantum Dot Light-Emitting Diodes for High Brightness and Stable Operation. ACS Nano 2020, 14, 17496–17504.

[12] Youngwoo Jeon; Soobin Sim; Doyoon Shin; Wan Ki Bae; Hyunkoo Lee; Hyunho Lee. All-Solution-Processed Top-Emitting InP Quantum Dot Light-Emitting Diode with Polyethylenimine Interfacial Layer. Adv. Electron. Mater. 2024, 10, 2400195.