Invited Paper 7.4 / H.-M. Kim

High-Efficiency Inverted Quantum-dot Light Emitting Diodes for Display

Hyo-Min Kim and Jin Jang

Advanced Display Research Center (ADRC) and Department of Information Display Kyung Hee University, Seoul 130-701, Korea

Abstract

We report the state-of-art technologies of quantum-dot light-emitting diodes, focused on the current and power efficiencies. And our recent results on QLEDs are also added. A high-efficiency inverted green quantum-dot light emitting diodes (QLEDs) was demonstrated in ADRC using stacked electron transporting layer (ETL), exhibiting maximum current efficiency of 28.29 cd/A and power efficiency of 22.11 lm/W, respectively. The additional ETL layer could improve the device performance by around 3 times compare to that of a QLED with single ETL.

Author Keywords

Inverted structure; quantum-dot; QLED; AMQLED;

1. Introduction

Quantum-dot light emitting diodes (QLEDs) are of increasing interest for wide color gamut display with high color purity. And, the color of QLEDs can be easily tuned by varying the core size of quantum-dots (QDs), such as Cd, Zn and In, without changing the device structure. However, QLEDs have the issues such as QD particle aggregation, material stability and uniform layer formation because of their small sizes under 10 nm. It is noted that uniform layer formation of QD layer is important to have high device performance such as current and power efficiencies. Therefore, the under-layer of QD should have a smooth surface morphology to have a uniform QD layer coating.

The schematic diagrams for regular and inverted QLEDs are shown in figure 1. Similar to OLEDs, regular and inverted QLEDs consist of hole injection layer (HIL), hole transporting layer (HTL), emissive layer (EML), electron transporting layer (ETL), electron injection layer (EIL), and top and bottom electrodes. The bottom electrodes of regular and inverted structures are used as anode and cathode, respectively.

Inverted structure of a device is useful for active-matrix (AM) organic light emitting diodes (OLEDs) and QLEDs with n-channel oxide thin-film transistors (TFT) such as Indiumgallium-zinc-oxide (IGZO). Oxide TFTs show mostly n-channel behavior and thus inverted structure of QLED with bottom cathode is preferred [1].

Recently, Shen et al, optimized shell thickness of QD and reported high efficiency QLED with regular structure exhibiting the power efficiency of 19.7 lm/W for green emission [2]. The shell thickness of QD affects the charge confinement in QD and charge injection in QDs. Therefore, the synthesis of QDs and device optimization are important to have high efficiency QLED.

In figure 2, current efficiency and external quantum efficiency (EQE) trends for QLEDs reported in the literatures are described. Figure 2 (a) and (b) show current efficiency trend of Cd-based and non Cd-based QLEDs, respectively [3]-[17]. As can be seen figure 2 (a), current efficiency of QLED is increasing steadily. In case of non Cd-based QLEDs, InP or ZnSe component are used as emission material. The device performance of red, green and blue emitting QLED is increasing every year, therefore, it can be similar to OLED in 5 to 10 years. In table 1, we summarized devices performance data for QLEDs

with conventional and inverted structures published in the Journals. The best maximum current efficiency and EQE reported for green are 19.2 cd/A and 5.8 %, respectively, by SNU [11]. And, those for red 19.2 cd/A and over 25.0 lm/W, respectively, by QD Vision in 2013 [12].

The inverted structure of QLED is well matched with oxide thin-film transistor (TFT) backplane. The first AMQLED was demonstrated at SID 2010 with 4 inch diagonal monochrome with a-Si:H TFT backplane [18]. All solution process of QLED could be possible so that large area AMQLED could be manufactured without using vacuum process. Note that current

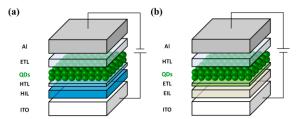


Figure 1. Schematic diagrams for (a) regular and (b) inverted QLEDs.

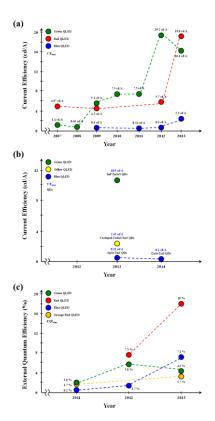


Figure 2. Current efficiency and EQE trend for the QLEDs reported in the literatures. Current efficiencies of (a) Cd based, (b) non Cd based QLEDs and (c) EQE trend of QLEDs.

7.4 / H.-M. Kim Invited Paper

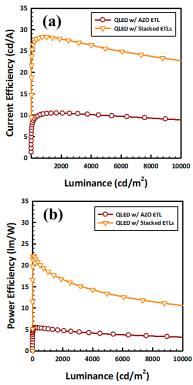


Figure 3. Device characteristics of inverted green QLED with stacked ETLs. (a) Current efficiency – luminance, and (b) power efficiency – luminance characteristics.

AMOLED TVs are manufactured with vacuum process. A full-color AMQLED was demonstrated at SID 2011 using printed QDs [19]. Therefore, the solution process for TFT backplane could be used for cost effective active-matrix QLED TV using printed red, green and blue QD diodes.

2. High efficiency inverted QLEDs

The charge transport layers for electron and hole should be optimized to have good charge balance [20], [21]. The barriers for electron and hole are also important to confine the carriers in the emission layer. Energy level alignment of a device is studied to achieve highly efficient device, with low charge injection barrier from electrode to EML [22]. Such as energy level alignment and decrease of charge injection barrier can be evaluated by studying electron and hole only devices. [23].

Al doped ZnO (AZO) layer was used as the electron transport layer [24] with device structure of ITO / AZO (~50 nm) / 2nd ETL (x nm) / CdSe/CdS/ZnS QDs (3.5~4.5 ML) / 4,4',4"-Tri(Ncarbazolyl) triphenylamine (TCTA) (10 nm) / N,N'bis(naphthalene-1-yl)-N,N'-bis(phenyl)- 2,2'demethylbenzidine (NPD) (20 nm) / Dipyrazino[2,3-f:2',3'-h]quinozaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) (20 nm) / Al (100 nm). An AZO layer was spin-coated at 2000 rpm onto ITO having a sheet resistance of 8~9 Ω/square and then annealed at 225°C for 10 min in ambient air. After annealing the AZO layer, 2nd ETL is formed by spin-casting method. And then, CdSe/CdS/ZnS green QDs, an average diameter of 6~7 nm, in toluene (concentration 10.0 mg/mL) was spin-coated at 3000 rpm and then heated at 190 °C for 10 min in a N₂ filled glove box. The TCTA layer acts as the hole transport and electron blocking layer (HTL and EBL) due to have lower lowest

unoccupied molecular orbital (LUMO) of 2.5 eV, NPD as a HTL and HAT-CN as a hole injection layer (HIL), all deposited by thermal evaporation. Then, Al (100 nm) layer was evaporated in vacuum on the top as anode. Finally, the devices were encapsulated with glass in a glove box with N₂ environment.

The current density-voltage (J-V), luminance-voltage (L-V) and PL spectra were measured using Konica Minolta CS100A luminance meter coupled with Keithley 2635A voltage and current source meter and SCINCO FS-2 fluorescence spectrometer.

Device characteristics of inverted green QLED studied in ADRC are shown in figure 3. Figure 3 (a) and (b) exhibit current efficiency versus voltage, and power efficiency versus voltage characteristics, respectively. In inverted green QLED, we adopted stacked ETL for reducing the energy level barrier.

Reducing energy level barrier is very important to fabricate high efficiency device. As can be seen in figure 3, device performance is improved significantly when we inserted additional layer between AZO and EML. Current and power efficiency of the stacked ETL based device were improved by 3 times compare to that of AZO based QLED. More details are shown in table 2. Our optimized device with stacked ETL has turn-on and driving voltages (V_T and V_D) of 2.41 and 3.70 V, respectively. And maximum current and power efficiency are 28.29 cd/A and 22.11 lm/W, respectively. When we inserted 2nd ETL on AZO, the device performances, such as current and power efficiency, were improved by around 3 times.

3. Summary for QLED efficiency

In table 2, we summarized the device performance data for inverted QLEDs manufactured in ADRC. We have studied on inverted structure QLEDs for AMQLED application. The effects of Al doping effect in ZnO, Cs₂CO₃ doping in Al doped ZnO

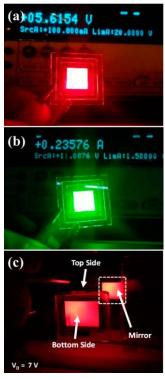


Figure 4. Operating images of (a) red, (b) green and (c) semi-transparent inverted QLEDs.

Invited Paper 7.4 / H.-M. Kim

Table 1 Device performances for Cd based	OLEDs with conventional and inverted structures appeared in literatures
Table 1. Device periormances for eu baseu	OLLD'S With Conventional and inverted structures appeared in incratures

Туре	Year	Color	C/E _{max} (cd/A)	P/E _{max} (lm/W)	EQE (%)	QLED structure	Ref#
Inverted	2013	Red	19.2	> 25.0	18	ITO/ZnONPs/R-QDs/NPB/HIL/Al	[12]
	2012	Deep-Red	5.7	N/A	7.3		
		Green	19.2	N/A	5.8	$ITO/ZnONPs/QDs/CBP/MoO_3/Al$	[11]
		Blue	0.4	N/A	1.7		
Conventional	2013	Yellow	$ \textbf{Yellow} \qquad \qquad 0.67 \qquad \qquad N/A \qquad \qquad N/A \qquad \qquad ITO / MoO_x / p - TPD / Y - QDs / Alq_3 / Ca:_A (1) / Alg_3 / Ca:_A (2) / Alg_3 / Ca:_A (3) / Alg_3 / Alg_$		$ITO / MoO_x / p\text{-}TPD / Y\text{-}QDs / Alq_3 / Ca\text{:}Al$	[25]	
		Blue	2.2	1.4	7.1	ITO / PEDOT:PSS / PVK / B-QDs / ZnO NPs / Al	[13]
		Green	16.4	19.7	4.1	ITO / PEDOT:PSS / TFB / ODs / ZnO NPs / Al	[2]
		Orange-Red	12.0	16.0	3.7	TIO/ PEDOT:PSS/ TFB / QDS/ ZHO NPS/ AI	[2]
		Orange-Red	3.9	3.8	1.7		
	2011	Green	7.5	8.2	1.8	ITO/PEDOT:PSS/p-TPD/QDs/ZnONPs/Al	[10]
		Blue	0.3	0.2	0.2		

Table 2. Device performances of the inverted OLEDs studied in ADRC.

Instanta d OLED	ETL Layers 1st 2nd		V _T (V)	V _D (V)	C/E _{max} (cd/A)	P/E _{max} (lm/W)	L (cd/m²)	@ 1,000 cd/m ²		@ 10,000 cd/m ²		Ref
Inverted QLED Concepts (Color)								C/E (cd/A)	P/E (lm/W)	C/E (cd/A)	P/E (lm/W)	#
Stacked ETL (G)	AZO	w/o	3.04	4.96	10.48	5.35	N/A	10.35	5.11	8.91	3.21	
		w/	2.41	3.70	28.29	22.11	N/A	28.28	18.59	22.76	10.60	
Stacked ETL (R)	AZO	w/o	1.61	2.59	3.32	4.15	N/A	3.09	2.52	1.87	0.86	-
		w/	1.62	2.45	7.55	10.96	N/A	6.49	5.82	4.37	2.22	
Al doping effect (R)	AZO		1.94	3.02	4.86	3.64	26,700	4.63	3.64	N/A	N/A	[24]
Cs ₂ CO ₃ doping effect (R)	AZO: Cs ₂ CO ₃		2.48	3.43	4.88	2.34	57,350	1.75	1.34	N/A	N/A	[21]
Semi-transparent (R)	Bottom Top		2.95	4.24	1.25	0.67	10,540	1.12	0.67	N/A	N/A	[26]
			3.03	4.61	0.54	0.27	2,800	0.53	0.27			
All solution processed	Re	ed	2.8	4.1	0.69	0.52	12,510					
inverted QLED (R, G, B)	Gre	en	3.6	4.9	2.81	1.08	32,370	N/A	N/A	N/A	N/A	[27]
	Blu	ıe	3.6	5.7	0.06	0.04	246					

(AZO) were studied. In addition, we demonstrated semi-transparent QLED [26] and also all solution processed QLED [27]. And figure 4 (a) \sim (c) shows operating images of red, green (1cm x 1 cm) and semi-transparent (one inch) inverted QLED, respectively.

4. Conclusion

We explained the state-of-art technology for QLEDs in terms of current and power efficiency. And, we have demonstrated high-efficiency inverted green QLED using stacked ETLs. Compare to single ETL based QLED, our device performance was improved by around 3 times. The V_T , V_D , maximum current and power efficiencies were found to be 2.41 V, 3.70 V, 28.29 cd/A and 22.11 lm/W, respectively.

5. Acknowledgements

This work was supported by the Human Resources Development program (No. 20134010200490) of the Korea

Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy.

6. References

- [1] S.Y. Chen, T.Y. Chu, J.F. Chen, C.Y.Su and C.H. Chen, "Stable inverted bottom-emitting organic electro-luminescent devices with molecular doping and morphology improvement" Applied Physics Letter 89, 053518-1-053518-3 (2006)
- [2] H. Shen, Q. Lin, H. Wang, L. Qian, Y. Yang, A. Titov, J. Hyvonen, Y. Zheng, and L.S. Li, "Efficient and Bright Colloidal Quantum Dot Light-Emitting Diodes via Controlling the Shell Thickness of Quantum Dots" ACS Applied Materials & Interfaces 5, 12011-12016 (2013)
- [3] Y.H. Niu, A.M. Munro, Y.J Cheng, Y. Tian, M.S. Liu, J. Zhao, J.A. Bardecker, I.J.-L Plante, D.S. Ginger, and A.K.-

7.4 / H.-M. Kim Invited Paper

- Y. Jen, "Improved Performance from Multilayer Quantum Dot Light-Emitting Diodes via Thermal Annealing of the Quantum Dot Layer" Advanced Materials **19**, 3371-3376 (2007)
- [4] Q. Sun, Y.A. Wang, L.S Li, D. Wang, T. Zhu, J. Xu, C. Yang, and Y. Li, "Bright, multicoloured light-emitting diodes based on quantum dots" Nature Phonics 1, 717-722 (2007)
- [5] J.W. Stouwdam and R.A. J. Janssen, "Red, green, and blue quantum dot LEDs with solution processable ZnO nanocrystal electron injection layers" Journal of Materials Chemistry 18, 1889-1894 (2008)
- [6] W.K. Bae, J. Kwak, J.W. Park, K. Char, C. Lee, and S. Lee, "Highly Efficient Green-Light-Emitting Diodes Based on CdSe@ZnS Quantum Dots with a Chemical-Composition Gradient" Advanced Materials 21, 1690-1694 (2009)
- [7] Q. Sun, G. Subramanyam, L. Dai, M. Check, A. Campbell, R. Naik, J. Grote and Y. Wang, "Highly Efficient Quantum-Dot Light-Emitting Diodes with DNA-CTMA as a Combined Hole-Transporting and Electron-Blocking Layer" ACS Nano 3, 737-743 (2009)
- [8] Z. Tan, J. Xu, C. Zhang, T. Zhu, F. Zhang, B. Hedrick, S. Pickering, J. Wu, H. Su, S. Gao, A.Y. Wang, B. Kimball, J. Ruzyllo, N.S. Dellas, and S.E. Mohney, "Colloidal nanocrystal-based light-emitting diodes fabricated on plastic toward flexible quantum dot optoelectronics" Journal of Applied Physics 105, 34312-1-34312-5 (2009)
- [9] B.H Kang, J.S Seo, S. Jeong, J. Lee, C.S Han, D.E Kim, K.J Kim, S.H Yeom, D.H. Kwon, H.R Kim, and S.W Kang, "Highly efficient hybrid light-emitting device using complex of CdSe/ZnS quantum dots embedded in copolymer as an active layer" Optics Express 18, 18303-18311 (2010)
- [10] L. Qian, Y. Zheng, J. Xue and P.H. Holloway, "Stable and efficient quantum-dot light-emitting diodes based on solution-processed multilayer structures" Nature Photonics 5, 543-548 (2011)
- [11] J. Kwak, W.K. Bae, D. Lee, I. Park, J. Lim, M. Park, H. Cho, H. Woo, D.Y. Yoon, K. Char, S. Lee, and C. Lee, "Bright and Efficient Full-Color Colloidal Quantum Dot Light-Emitting Diodes Using an Inverted Device Structure" Nano Letter 12, 2362-2366 (2012)
- [12] B.S. Mashford, M. Stevenson, Z. Popovic, C. Hamilton, Z. Zhou, C. Breen, J. Steckel, V. Bulovic, M. Bawendi, S.C. Sullivan and P.T. Kazlas, "High-efficiency quantum-dot light-emitting devices with enhanced charge injection" Nature Photonics 7, 407-412 (2013)
- [13] K.H. Lee, J.H Lee, W.S. Song, H. Ko, C. Lee, J.H Lee, and H. Yang, "Highly Efficient, Color-Pure, Color-Stable Blue Quantum Dot Light-Emitting Devices" ACS Nano 7, 7295-7302 (2013)
- [14] J. Lim, M. Park, W.K. Bae, D. Lee, S. Lee, C. Lee, and K. Char, "Highly Efficient Cadmium-Free Quantum Dot Light-Emitting Diodes Enabled by the Direct Formation of Excitons within InP@ZnSeS Quantum Dots" ACS nano 10, 9019-9026 (2013)
- [15] W. Ji, P. Jing, W. Xu, X. Yuan, Y. Wang, J. Zhao, and

- Alex. K. –J. Jen, "High color purity ZnSe/ZnS core/shell quantum dot based blue light emitting diodes with an inverted device structure" Applied Physics Letters **103**, 053106-1-053106-4 (2013)
- [16] C. Ippen, T. Greco, Y. Kim, J. Kim, M.S. Oh, C.J. Han, and A. Wedel, "ZnSe/ZnS quantum dots as emitting material in blue QD-LEDs with narrow emission peak and wavelength tenability" Organic Electronics 15, 126-131 (2014)
- [17] W. Zhang, Q. Lou, W. Ji, J. Zhao, and X. Zhong, "Color-Tunable Highly Bright Photoluminescence of Cadmium-Free Cu-Doped Zn-In-S Nanocrystals and Electroluminescence" Chemistry of Materials 26, 1204-1212 (2014)
- [18] P.T. Kazlas, Z. Zhou, M. Stevenson, Y. Niu, C. Breen, S.J Kim, J.S. Stecket, S. Coe-Sullivan, and J. Ritter, "Quantum Dot Light Emitting Diodes for Full-color Active-matrix Displays" SID Symposium Digest of Technical Papers 41, 473-476 (2010)
- [19] S. Coe-Sullivan, Z. Zhou, Y. Niu, J. Perkins, M. Stevenson, C. Breen, P.T. Kazlas and J.S. Steckel, "Quantum Dot Light Emitting Diodes for Near-to-eye and Direct View Display Applications" SID Symposium Digest of Technical Papers 42, 135-138 (2011)
- [20] V. Wood, M. J. Panzer, J. E. Halpert, J.-M. Caruge, M. G. Bawendi, and V. Bulovic, "Selection of Metal Oxide Charge Transport Layers for Colloidal Quantum Dot LEDs" ACS Nano 3, 3581-3586 (2009)
- [21] H.M Kim, A.B.R.M Yusoff, J.H Youn and J. Jang, "Inverted quantum-dot light emitting diodes with cesium carbonate doped aluminium-zinc-oxide as the cathode buffer layer for high brightness" Journal of Materials Chemistry C 1, 3924-3930 (2013)
- [22] H. Lee, C.M Kang, M. Park, J. Kwak, and C. Lee, "Improved Efficiency of Inverted Organic Light-Emitting Diodes Using Tin Dioxide Nanoparticles as an Electron Injection Layer" ACS Applied Materials & Interfaces 5, 1977-1981 (2013)
- [23] B. Kumar, R. Hue, W.L. Gladfelter, and S.A. Campbell. J, "Comparing direct charge injection and Forster energy transfer into quantum dots in hybrid organic/inorganic quantum dot light emitting devices" Journal of Applied Physics 112, 034501-1-034501-5 (2012)
- [24] H.M Kim, J.H Youn, G.J Seo and J. Jang, "Inverted quantum-dot light-emitting diodes with solution-processed aluminium–zinc oxide as a cathode buffer" Journal of Materials Chemistry C 1, 1533-1688 (2013)
- [25] S. He, S. Li, F. Wang, A.Y. Wang, J. Lin, and Z. Tan, "Efficient quantum dot light-emitting diodes with solutionprocessable molybdenum oxide as the anode buffer layer" Nanotechnology 24, 175201-175207 (2013)
- [26] H.M. Kim, A.B.R.M. Yusoff, T.W. Kim, Y.G. Seol, H.P. Kim, and J. Jang, "Semi-transparent quantum-dot light emitting diodes with an inverted structure" Journal of Materials Chemistry C 2, 2259-2265 (2014)
- [27] A. Castan, H.M. Kim, and J. Jang, "All-Solution-Processed Inverted Quantum-Dot Light-Emitting Diodes" ACS Applied Materials & Interfaces 6, 2508-2515 (2014)