High-performance tandem CdSe/ZnS quantum-dot light-emitting diodes with a double-layer interconnecting layer composed of thermally evaporated and sputtered metal oxides

Ohun Kwon, Dongjin Kim, Mijin Kim and Honyeon Lee

Department of Electronic Materials, Devices and Equipment Engineering, Soonchunhyang University, Asan, Korea

ABSTRACT
High-performance tandem quantum-dot light-emitting diodes (QLEDs) are needed for practical next-generation displays. This study designed a high-performance interconnecting layer (ICL) that combines QLED units into tandem QLEDs and demonstrated its effectiveness. The ICLs were designed for charge generation, for interconnecting QLEDs, and for protecting the underlayers from damage during upper-layer fabrication. Using the ICLs with a first layer of thermally evaporated WO3 and a second layer of sputtered SnO2 or zinc tin oxide, the required roles of the ICL were fulfilled. The current efficiencies of tandem QLEDs using a double-layer ICL were about triple those of a single QLED, an improvement from 26 cd/A for a single QLED to 82 cd/A for a tandem QLED connecting two QLED units. This current efficiency was much higher than previously reported values for tandem QLEDs connecting QLED units with CdSe/ZnS green quantum dots and ZnO electron-transport layers. The method presented here will contribute to the practical application of QLEDs for large TVs and light-illumination devices.

1. Introduction
The electronic display devices industry is progressing rapidly, with liquid crystal displays (LCDs) being the current standard and are used in most applications. However, organic light-emitting diodes (OLEDs) have been applied in high-end mobile devices and televisions (TVs) because of their superior self-emissive display performance compared to non-self-emissive LCDs [1]. Despite the superior display performance of OLEDs, they are not very reliable. Organic emissive materials are vulnerable to environmental problems [2] that compromise OLED reliability. Quantum-dot light-emitting diodes (QLEDs) featuring colloidal inorganic quantum dots (QDs) are designed to address such reliability issues [3]. In addition, the color purity of QLEDs is much better than the color purity of OLEDs [4] because of the quantum confinement effects unique to QDs [5,6]. Thus, QLEDs offer considerable potential as next-generation display technology. In the laboratory, QLED performance is now almost comparable to that of OLEDs [7,8]. However, a few issues (including tandem QLED technologies) remain prior to practical QLED applications. Tandem devices are appropriate for large, high-brightness, and low-cost devices (e.g. large TVs and surface illuminations [9,10]). An OLED TV features a technology that derives three primary color lights from a white or blue light. White light is created in tandem devices featuring red, green, and blue unit devices [11], or orange-green and blue unit devices [12]. These white-light tandem devices can also be used for surface illumination. A blue-light device can serve as a light source for color conversion [13], although in this context, a tandem blue-light device is required to ensure sufficient brightness [14]. It is difficult to obtain reliable high-performance tandem QLEDs principally owing to underlayer damage caused by the QD solvent [15]. During QD emission layer (EML) fabrication, the QD solvent damages underlayers and reduces device performance. Here, we sought a way to come up with a high-performance tandem QLED by examining the effects of the interconnecting layer (ICL) that connects two QLED units to form a tandem QLED. The basic role of an ICL is to generate charge carriers and supply them to both of the QLED units. We added the role of protecting underlayers to the ICL and designed the necessary ICL structures and fabrication processes. We studied the effects of the designed ICLs by examining the properties...
of tandem QLEDs with ICLs. Through this approach, we were able to fabricate a high-performance tandem QLED. The detailed results are presented and discussed below.

2. Experiments

Tandem QLEDs composed of two QLED units were fabricated with an inverted stacked structure (i.e., a bottom cathode and a top anode). The device layers consisted of indium tin oxide (ITO) (150 nm)/ZnO (25 nm)/CdSe/ZnS QDs (9 nm)/di-[4-(N,N-di-p-tolyl- amino)-phenyl]cyclohexane (TAPC) (50 nm)/ICL/ZnO NP (25 nm)/QD (9 nm)/WO3 (9 nm)/Ag (100 nm) (Figure 1(a)). On a glass substrate, a 150-nm ITO transparent bottom cathode was deposited by sputtering and was patterned using photolithography. On the ITO cathode, a 25-nm ZnO NP electron transport layer (ETL) was deposited by spin-coating ZnO NPs dispersed in ethanol. On the ETL, a 9-nm EML was deposited by spin-coating the CdSe/ZnS core/shell green QDs dispersed in heptane. The CdSe/ZnS QDs with oleic acid ligands (9-nm diameter) were from Global Zeus (Korea). The QDs had a photoluminescence (PL) peak wavelength of 525 nm and full-width at half-maximum of < 35 nm. The PL quantum yield was > 85%. The surface morphology of a QD EML is shown in Figure 1(b), which shows a 3 × 3-μm² atomic force microscopy (AFM) image of a QD EML on a ZnO NP ETL. On the EML, a 50-nm TAPC hole-transport layer (HTL) was deposited by vacuum thermal evaporation. A bottom QLED unit (from the ITO cathode to the TAPC HTL) was fabricated using the processes described above. On the bottom QLED unit, an ICL was fabricated. Two types of ICL were tested: a single-layer ICL (an in vacuo thermal-evaporated 11-nm WO3 layer) and a double-layer ICL (an in vacuo thermal-evaporated 11-nm WO3 layer and a sputtered metal oxide layer). Zinc tin oxide (ZTO), SnO2, and NiO were used as sputtered metal oxide layers. The surface morphologies of the sputtered layers are shown in Figure 1(c)–(e), which are 5 × 5-μm² AFM images of 60-nm-thick SnO2, NiO, and ZTO films on glass substrates. On the ICL, a top QLED unit was fabricated. The structure and processes of the top QLED unit were the same as the structure and processes of the bottom QLED unit. On the top TAPC HTL, a hole injection layer (HIL) of 10-nm WO3 and an anode of 100-nm Ag were deposited sequentially by vacuum thermal evaporation. The patterns of all layers except the ITO cathode were obtained using metal shadow masks during the deposition processes. The electroluminescence (EL) emission spectrum of the fabricated QLED and the PL emission spectrum of the CdSe/ZnS QD are shown in Figure 1(f), where the EL peak position has red-shifted by 4 nm from the PL peak position because of a quantum-confined Stark effect [16].

Figure 1. (a) Schematic of tandem QLEDs. AFM surface images of (b) QD EML (on a ZnO NP ETL), (c) SnO2, (d) NiO, and (e) ZTO. (f) The EL emission spectrum of a fabricated QLED and the PL emission spectrum of CdSe/ZnS QD. (g) The current density curves of a single QLED and tandem QLEDs; SnO2, ZTO, and NiO refer to tandem QLEDs with 40-nm-thick SnO2, ZTO, and NiO layers, respectively.
The current-voltage curves of tandem QLEDs are compared to the current-voltage curves of a single QLED in Figure 1(g).

The QLED current-voltage-luminance (I-V-L) characteristics were measured using an I-V-L tester (Polaronix M6100IVL; McScience, Korea) combined with a spectroradiometer (Spectrascan-PR650; Photo Research, USA). To analyze the energy band levels, the study performed ultraviolet photoelectron spectroscopy (UPS; AXIS Ultra DLD; Kratos Analytical, UK) and ultraviolet-visible (UV-Vis) spectroscopy (UV-PC1650; Shimadzu, Japan). The AFM surface images were obtained using the XE-7 device of Park Systems Corp. (Korea).

3. Results and discussion

A single QLED was fabricated on a glass substrate and used as the reference device for evaluating the tandem QLED. The device layers consisted of an ITO cathode (150 nm)/ZnO NP ETL (25 nm)/QD EML (9 nm)/TAPC HTL (50 nm)/WO3 HIL (9 nm)/Ag cathode (100 nm). The layer thicknesses of the single QLED were determined in previous experiments to optimize the single device structure. As shown in Figure 2, the single QLED performed well, with 3.0 × 10^4 cd/m^2 luminance and 26 cd/A current efficiency. These values are higher than those yielded by previous reports on QLEDs with the same EML and ETL materials similar to the materials used in this study [17–19]. To fabricate the tandem QLEDs, thermally evaporated WO3 and sputtered ZTO, SnO2, and NiO were tested as single-layer ICLs. However, light was not emitted from tandem devices with an ICL comprising a sputtered single layer, while weak light was emitted only from the tandem device with a thermally evaporated WO3 ICL. Figure 2 shows the properties of the tandem QLED with the WO3 ICL; the luminance and current efficiencies of the tandem QLED were lower than those of the single QLED. The inability of the tandem devices with sputtered ICLs to emit light may be explained by the damage to the underlayers during ICL sputtering. The poor performance of the tandem device with the thermally evaporated WO3 ICL may be explained by underlayer damage caused by the QD solvent. To overcome these problems, double-layer ICLs were designed and their effects on tandem QLED performance were examined.

The double-layer ICLs were designed with a first layer of thermally evaporated WO3 and a second layer of sputtered metal oxide. The thermally evaporated WO3 first layer was placed on the organic TAPC HTL to generate charge carriers and prevent sputtering damage during second layer deposition; the sturdy sputtered metal oxide second layer was placed on the first layer to protect the underlayers from the QD solvent. A double-layer ICL was expected to improve tandem QLED performance by combining the effects of the first and second layers. Figure 3 shows the properties of tandem QLEDs with a WO3/SnO2 double-layer ICL. The SnO2 thickness was varied from 25 to 60 nm; the thicker SnO2 layer resulted in greater luminance and current efficiency. With the 11-nm WO3/60-nm SnO2 ICL, the tandem QLED had a current efficiency of 66 cd/A, which was 2.5 times that of a single QLED. This improved performance with the SnO2 layer proved the effectiveness of a double-layer ICL.

Figure 4 shows the properties of tandem QLEDs with WO3/ZTO double-layer ICLs. The ZTO thickness varied from 25 to 60 nm. A thinner ZTO layer afforded higher luminance and current efficiency. The tandem QLED with an 11-nm-thick WO3/25-nm-thick ZTO ICL

![Figure 2. Luminance (a) and current efficiency (b) curves as functions of the current density of the (reference) single QLED and a tandem QLED with a single-layer ICL of thermally evaporated WO3.](image-url)
layer exhibited a current efficiency of 82 cd/A, which is 3.2-fold greater than the current efficiency of the single QLED. This efficiency was much better than the previously reported efficiencies of green tandem QLEDs with a CdSe/ZnS EML and a pure ZnO ETL (< 60 cd/A) [20]. The EML and ETL materials greatly affect device performance; we thus evaluated the effects of our double-layer ICLs on device efficiencies, comparing them to the efficiencies of tandem QLEDs fabricated from the EML and ETL materials used here. The improved performance of tandem QLEDs with ZTO layers clearly demonstrated the utility of a double-layer ICL.

Figure 5 shows the properties of tandem QLEDs with a WO3/NiO double-layer ICL. The NiO thickness was varied from 25 to 60 nm. The thinner NiO layer resulted in greater luminance and current efficiency. For the 11-nm WO3/25-nm NiO ICL, the tandem QLED had a current efficiency of 32 cd/A, which was 1.2 times that of the single QLED. The tandem QLED operated stably compared to the tandem QLED with a WO3 single-layer ICL, demonstrating that the NiO second layer protected the underlayers from QD solvent damage. However, the improved efficiency of the tandem QLEDs composed of two QLED units did not meet our study’s expectations of reaching twice the current efficiency of a single QLED.

The difference in tandem QLED performance associated with double-layer ICL materials can be understood by considering the energy levels of the ICL layers as shown in Figure 6. The TAPC, WO3, ZTO, and NiO energy levels were extracted from our UPS and UV-Vis analyses, while the levels of SnO2 were from previous reports [21–23]. There are no electron injection barriers from the WO3 first layer into the SnO2 and ZTO.
second layers, as shown in Figure 6(a) and (b). However, there is a large electron injection barrier from the WO₃ first layer into the NiO second layer, as shown in Figure 6(c). This explains the high performance of the tandem QLEDs having double-layer ICLs with SnO₂ or ZTO second layers compared to the double-layer ICL with an NiO second layer.

The current density curves of tandem QLEDs were the curves of space-charge limited currents (SCLCs) with exponentially distributed traps [24]. An SCLC with such traps can be described by the following formula:

$$J \propto V^{T_c/T+1},$$

where $J$, $V$, $T$, and $T_c$ are the current density, bias voltage, temperature, and trap characteristic temperature, respectively. The trap density is:

$$n_{\text{trap}}(E) \propto T_c^{-1} \exp(-E/k_BT_c),$$

where $n_{\text{trap}}$, $E$, and $k_B$ are the trap density, trap energy, and Boltzmann constant, respectively. The slopes of the curves in Figure 7 reflect the $T_c/T + 1$ values of Equation (1). The $T_c$ values extracted from the slopes are shown as insets of Figure 7. A larger slope indicates a higher $T_c$ and a wider trap distribution (Equation (2)). A narrower trap distribution (a smaller slope in Figure 7) reflects better device efficiency. It is not clear yet what factors affect the dependence of the trap distribution on the film thickness.

As described above, a double-layer ICL noticeably improved the tandem QLED performance. The current efficiencies of the tandem QLEDs with SnO₂ or ZTO second layers were about triple that of a single QLED, exceeding the expected improvement. A tandem device connecting two devices should normally have a current efficiency twice that of a single device. The greater efficiency improvement can be explained by the charge carrier balance. The electron supply to QD EMLs generally surpasses the hole supply for QLEDs with a ZnO NP ETL and a CdSe/ZnS QD EML [18,25]; this charge supply imbalance compromises QLED performance. The charge balance of the upper QLED unit can be improved by using a double-layer ICL. The electrons of the upper QLED unit are supplied by the ICL, so the electron supply is restricted by the charge generation rates at the ICL and TAPC HTL interface. This restricted electron supply reduces the charge supply imbalance and improves the current efficiency.
4. Conclusions

In this study, we designed and fabricated double-layer ICLs with excellent performance for tandem QLEDs. The ICLs consisted of a thermally evaporated WO$_3$ first layer and a sputtered metal oxide second layer. The WO$_3$ first layer generates charge carriers and protects lower organic layers from sputtering damage during second layer deposition. The charge carriers are generated at the interface between the WO$_3$ first layer and TAPC HTL. The metal oxide second layer protects the underlayers from the QD solvent and transports the generated electrons into the upper QLED unit. For smooth electron transport into the upper QLED unit, we expected no injection barriers between the first and second layers. No such injection barriers occurred as the the SnO$_2$ and ZTO layers had suitable energy levels based on our UPS and UV-Vis analyses. The current efficiencies of the tandem QLEDs using a double-layer ICL were approximately triple that of a single QLED. This study thus demonstrated a method to solve the essential issues for obtaining high-performance tandem QLEDs, a finding that should contribute to practical applications of QLEDs for large-area TVs and light-illumination devices. However, the results of our study indicated that further work is needed for a better understanding of the charge carrier behaviors of double-layer ICLs and ICL optimization.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by a grant of the Korea Institute for Advancement of Technology (KIAT) jointly funded by the Korea Government (MOTIE) (P0012453, The Competency Development Program for Industry Specialist) and the Soonchunhyang University Research Fund.

Notes on contributors

Ohun Kwon received an M.Sc. in 2022 from the Department of Electronic Materials, Devices, and Equipment of the Soonchunhyang University in Asan, South Korea. He has been doing research on tandem quantum-dot light-emitting diodes.

Dongjin Kim is a postdoctoral researcher at Soonchunhyang University from which he received a Ph.D in 2022 from its Department of Electronic Materials, Devices, and Equipment. He has been conducting research on organic light-emitting diodes and quantum-dot light-emitting diodes.

Mijin Kim received an M.Sc. in 2022 from Soonchunhyang University's Department of Electronic Materials, Devices, and Equipment. She has been doing research on flexible quantum-dot light-emitting diodes.

Honyeon Lee received a Ph.D in 1997 from the Department of Physics of the Korea Advanced Institute of Science and Technology (KAIST) in Daejeon, South Korea. He subsequently conducted research on display technologies at Hyundai Electronics, SK Hynix, and Samsung Electronics. Since 2006, he has been a professor at the of Soonchunhyang University’s College of Engineering.
References

[1] S.-J. Zou, Y. Shen, F.-M. Xie, J.-D. Chen, Y.-Q. Li, and J.-X. Tang, Mater. Chem. Front 4, 788 (2020). doi:10.1039/c9qm00716d.

[2] T.E. Huang, H.J. Chen, C.H. Chen, Y.H. Lin, S.Z. Chen, S.W. Wen, and J.H. Jou, Org. Electron 99, 106333 (2021). doi:10.1016/j.orgel.2021.106333.

[3] Y. Sun, Y. Jiang, X.W. Sun, S. Zhang, and S. Chen, Chem. Rec 19, 1729 (2019). doi:10.1002/tcr.201800191

[4] V. Wood, and V. Bulović, Nano Rev 1, 5202 (2010). doi:10.3402/nano.v1i0.5202

[5] H. Lu, G.M. Carroll, N.R. Neale, and M.C. Beard, ACS Nano 13, 939 (2019).

[6] B.O. Dabbousi, J. Rodriguez-Viejo, F.V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.F. Jensen, and M.G. Bawendi, J. Phys. Chem. B 101, 9463 (1997). doi:10.1021/jp971091y

[7] W.K. Bae, and J. Lim, Korean J. Chem. Eng 36, 173 (2019). doi:10.1007/s11814-018-0193-7

[8] T. Lee, B.J. Kim, H. Lee, D. Haehm, W.K. Bae, J. Lim, and J. Kwak, Adv. Mater 34, 2106276 (2021). doi:10.1002/adma.202106276

[9] M.K. Fung, Y.Q. Li, and L.S. Liao, Adv. Mater 28, 10381 (2016). doi:10.1002/adma.201601737

[10] H. Zhang, Q. Su, and S. Chen, J. Inf. Disp 20, 169 (2019). doi:10.1080/15980316.2019.1650129

[11] M.J. Park, Y.H. Son, H.I. Yang, S.K. Kim, R. Lampande, and J.H. Kwon, ACS Photonics 5, 655 (2018). doi:10.1021/acsphotonics.7b01379

[12] H. Cho, C.W. Byun, C.M. Kang, J.W. Shin, B.H. Kwon, S. Choi, N.S. Cho, J.I. Lee, H. Kim, J.H. Lee, M. Kim, and H. Lee, J. Inf. Disp 20, 249 (2019). doi:10.1080/15980316.2019.1671240

[13] S.C. Dong, Y. Jiang, and C.W. Tang, J. Soc. Inf. Disp 29, 961 (2021). doi:10.1002/jsid.1072

[14] Y. Liu, X. Wu, Z. Xiao, J. Gao, J. Zhang, H. Rui, X. Lin, N. Zhang, Y. Hua, and S. Yin, Appl. Surf. Sci 413, 302 (2017). doi:10.1016/j.apsusc.2017.04.038

[15] H. Zhang, S. Chen, and X.W. Sun, ACS Nano 12, 697 (2018). doi:10.1021/acsnano.7b07867

[16] H. Lee, J. Semicond. Disp. Technol 20, 11 (2021).

[17] B.-H. Kang, J.-S. Lee, S.-W. Lee, S.-W. Kim, J.-W. Lee, S.-A. Gopalan, J.-S. Park, D.-H. Kwon, J.-H. Bae, H.-R. Kim, and S.-W. Kang, Sci. Rep 6, 34659 (2016). doi:10.1038/srep34659

[18] W. Zhang, L. Yang, Q. Zhang, Y. Zhang, F. Li, C. Chang, H. Sun, M. Yang, S. Yanto, and Z. Zhang, IEEE Trans. Electron Devices 66, 4901 (2019). doi:10.1109/TED.2019.2937788

[19] D. Li, Y. Yuan, K. Xu, X. Xue, J. Xu, H. Wang, S. Li, L. Wang, Z. Lu, and X. Zhang, Semicond. Sci. Technol 35, 055036 (2020). doi:10.1088/1361-6641/ab7a40

[20] P. Shen, F. Cao, H. Wang, B. Wei, F. Wang, X.W. Sun, and X. Yang, ACS Appl. Mater. Interfaces 11, 1065 (2019). doi:10.1021/acsami.8b18940

[21] D.O. Scanlon, and G.W. Watson, J. Mater. Chem 22, 25236 (2012). doi:10.1039/c2jm34352e

[22] A.M. Ganose, and D.O. Scanlon, J. Mater. Chem. C 4, 1467 (2016). doi:10.1039/C5TC04089B

[23] B. Höfling, A. Schleife, C. Rödl, and F. Bechstedt, Phys. Rev. B 85, 035305 (2012). doi:10.1103/PhysRevB.85.035305

[24] P. Zhang, Y.S. Ang, A.L. Garner, Á Valfells, J.W. Luginsland, and L.K. Ang, Appl. Phys 129, 100902 (2021). doi:10.1063/5.0042355

[25] D.J. Kim, and H.N. Lee, Jpn. J. Appl. Phys 58, 106502 (2019). doi:10.7567/1347-4065/ab3c77