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Performance improvement of blue quantum dot light-emitting diodes by facilitating electron transportation and suppressing electroplex emission

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ABSTRACT

The enhanced device performance of blue quantum dot light-emitting diodes (QD-LEDs) was demonstrated; a positive aging process was used to improve electron transport and suppress electroplex emission, which results from the interface between the QD-emitting layer and the ZnO electron-transporting layer (ETL). This electroplex interface functions as a low-energy recombination center, leading to energy loss and further decreasing the device performance. Without the positive aging process, the QD-LED exhibited poor electrical and electroluminescent (EL) characteristics, as well as an EL spectrum containing a strong electroplex emission with a peak at 635 nm. A positive aging process was applied by dripping a surface active reagent on the cathode before device encapsulation. The active reagent treatment led to suppression of the electroplex emission and enhanced device performance by promoting Al atoms into ZnO ETL to facilitate electron transport at the QD/ZnO interface. Furthermore, static positive aging was investigated by assessing the QD-LEDs at different storage times to observe the maturing process. After 409-hrs of maturing, the QD-LEDs exhibited an optimal device performance with favorable CE_{max} and EQE_{max} values of 6.2 cd/A and 8.7%, respectively. At a current density of 1 mA/cm², the QD-LED exhibited a maximum overall efficiency enhancement factor of 7.1 after the positive aging process.

1. Introduction

Quantum dot light-emitting diodes (QD-LEDs or QLEDs) have attracted a great deal of attention and have been widely investigated in the past few years because of their superior properties, such as high color purity, size-dependent emission spectrum, low operating voltage, high brightness, and low-cost fabrication [1–7]. QD-LED device performance, especially efficiency, has been successfully enhanced through improvements in the QD material properties and modifications to device structure. Thus, QD-LEDs are considered a promising candidate for nextgeneration display technology. The typical device configuration principally consists of a key QD emission layer inside a cascaded device. Similar to organic LEDs, the basic principle of QD-LEDs is that carriers are injected from their respective electrodes through p-type and n-type transporting layers and recombine in the QD layer, thereby emitting photons [8]. Furthermore, several QD materials have reported, including the II-VI group (CdSe, CdS, ZnSeS), the III-V group (InP, GaP, GaInP₂, InAs, and GaAs), and the perovskite base (CsPbX₃, X = Cl, Br, I), that are particularly promising [9–11].

Devices used for flat display applications require low operating voltage, high current efficiency, and high external quantum efficiency [12–16]. Therefore, numerous studies have explored improving QD material and device architecture in the last decade [17–28]. In a typical QD-LED, zinc oxide (ZnO) is used as the electron transport layer (ETL) to achieve high efficiency. However, ZnO has a high work function contact with QDs, and thus QD quenching can occur because of interfacial charge transport, which decreases efficiency. Therefore, Sun et al. proposed Al-doped ZnO (AZO, doping ratio 10% Al content) to replace ZnO

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Received 10 September 2020; Received in revised form 13 November 2020; Accepted 30 November 2020 Available online 4 December 2020 1385-8947/© 2020 Elsevier B.V. All rights reserved. as the ETL, which would enable the energy level to be raised to suppress charge transfer at the QD/ETL interface. These devices exhibited large enhancements in the current efficiency (CE) and external quantum efficiency (EQE) [27].

Generally, device performance degrades with an increase in storage time. However, positive aging has been reported to improve device performance [29–32]. For instance, Su et al. reported that the EQE_{max} increased by 1.6-fold for blue QD-LEDs when an acidic resin was applied as an encapsulation layer in the fabrication of QD-LEDs with a normal structure. Furthermore, lower leakage current and operational voltage were also observed, which the researchers speculated originated from the interfacial reaction between ZnMgO (n-layer) and the Al cathode, resulting in the formation of alloyed AlZnMgO interface and the improvement of ZnMgO conductivity [30]. Moreover, Acharya et al. observed a positive aging effect and concluded that positive aging is a result of the encapsulation resin reacting with ZnO to form carbonate, which could reduce ZnO defect densities [29].

Electroplex refers to a type of charge-transfer complex emission produced by the interaction of the hole on the highest occupied molecular orbital (HOMO) of the donor and the electron on the lowest unoccupied molecular orbital (LUMO) of the acceptor to form a radical ion pair [33–35]. Thus, optical transitions between the HOMO and LUMO levels can occur through a similar mechanism as exciplex [33]; however, an electroplex is only observed in electroluminescence (EL), whereas an exciplex can be observed both in EL and photoluminescence (PL).

In this study, a great improvement in QD-LED performance utilizing the time-dependent positive aging treatment was demonstrated by dripping an active reagent on the surface of the Al cathode and waiting for a period of time. In addition, we investigated not only the active reagent action, but also the detailed carrier dynamics and material changes during the time-dependent positive aging in the blue QD-LED. Without the active reagent, a reference QD-LED showed worse device performance and an emission spectrum containing an obvious electroplex emission as reported by Chen et al. [36,37]. The active reagent reaction utilized acrylic acid to enable Al atoms to penetrate into the ZnO ETL and form the AZO ETL, which reduced the energy barrier at the QD/ETL interface, facilitated electron transport into QD layer, reduced the driving voltage and benefited the device performance. In particular, a decrease in the intensity of electroplex emission could be observed because of the active reagent modification of the QD/ETL interface. Further evidence of Al content penetration into ZnO layer was obtained by depth-profiling X-ray photoelectron spectroscopy (XPS) analysis, which also could explain the energy level changes due to the material transformation from ZnO to AZO. With increasing storage time periods, the static positive aging process matured and led to improved QD-LED performance.

2. Experimental section

2.1. Device information

The structure of the QD-LEDs was indium tin oxide (ITO)/poly(3,4ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (30 nm)/poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,40-(N-(4-*sec*-butylphenyl) diphenylamine)] (TFB) (22 nm)/poly(9-vinylcarbazole) (PVK) (35 nm)/blue CdSe-based QD (18 nm)/ZnO (36 nm)/aluminum (Al) (100 nm), with ITO as an anode, PEDOT:PSS as a hole injection layer (HIL), TFB as the first hole transporting layer (HTL), PVK as the second HTL and electron blocking layer (EBL), CdSe-based QD (CdZnSeS core/ ZnS shell/OT with a size ~10.5 nm, quantum yield ~85% [24,27,30]) as an emitting layer (EML), ZnO as an ETL, electron injection layer and hole blocking layer, and Al as a cathode. Except for the anode and cathode, the layers were deposited using a spin coating process in a glovebox. The PEDOT:PSS layer was coated onto a ITO substrate (spun at 720 rpm for 1 min, annealed at 230 °C for 15 min); the TFB layer was coated on the



Fig. 1. (a) Cross-section TEM image, (b) energy level of each layer for blue QD-LEDs.

PEDOT:PSS layer (3700 rpm for 1 min, 230 °C for 30 min); the PVK layer was coated on the TFB layer (4000 rpm for 1 min, 150 °C for 30 min); the QD layer was coated on the PVK layer (2000 rpm for 1 min); ZnO was coated on the QD layer (2000 rpm for 40 sec, 70 °C for 30 min). The ITO glass substrate was a commercial product with a sheet resistance of 30 Ω /sq. The Al layer was deposited using thermal evaporation under a high vacuum of approximately 9×10^{-6} torr. The emission area of the QD-LED defined by ITO pattern and Al mask is 2×2 mm². After the Al cathode deposition, the device was encapsulated in a glovebox as a reference QD-LED fabrication process. For the positive aging treatment, a drop of the active reagent, acrylic acid, was applied to the Al cathode surface before device encapsulation. The device was then static stored. The CdSe-based QD, ZnO, and surface active reagent were supplied by Mesolight Inc.

2.2. Measurement

To characterize the device EL, a luminance–current density–voltage (L–J–V) measurement system was applied. The system comprised a multisource meter (Keithley 2400), a spectrometer (Minolta CS-1000), and a computer with control software. A fluorescence spectrometer (Hitachi FL4500) was employed to measure the steady-state PL spectra from the ETL, HTL, and QDs. Transient electroluminescence (TREL) measurement was employed to observe carrier and exciton behavior in the QLED. The setup consisted of a waveform function generator (Agilent 335011B) to drive the device, a photomultiplier (Hamamatsu H6780-20) and an oscilloscope (Tektronix TSB2202B) to collect the optical emission from the QLED. A transient PL (TRPL) setup, using a second-harmonic generation of a femtosecond Ti:sapphire pulse laser



Fig. 2. (a) L–J–V curves, (b) CE-J and EQE-J curves, (c) normalized EL spectra at 4.4 V and highlighted electroplex emission spectra (inset) of reference and activereagent QD-LEDs, and (d) PL spectra of QD, ZnO, and QD/ZnO films.

Table 1

Device	Time (h)	^{a)} Voltage (V)	λ _P (nm)	CIE (x,y)	FWHM (nm)	CE (cd/A)	EQE (%)
Reference.	0 97 409 602	4.6 4.3 4.4 4.5	464	(0.15, 0.06) (0.15, 0.06) (0.15, 0.06) (0.15, 0.06)	20	$0.9^{b)}, 0.9^{c)}$ $0.7^{b)}, 0.6^{c)}$ $0.7^{b)}, 0.7^{c)}$ $0.8^{b)}, 0.8^{c)}$	$\begin{array}{c} 1.2^{\rm b)}, 1.1^{\rm c)} \\ 0.9^{\rm b)}, 0.7^{\rm c)} \\ 0.9^{\rm b)}, 0.8^{\rm c)} \\ 1.0^{\rm b)}, 1.0^{\rm c)} \end{array}$
Active reagent	0 97 409 602	3.4 3.1 3.2 3.1	464	(0.14, 0.05) (0.14, 0.05) (0.14, 0.05) (0.14, 0.05)	21	$3.5^{b)}, 1.4^{c)}$ $5.4^{b)}, 4.0^{c)}$ $6.2^{b)}, 5.6^{c)}$ $5.6^{b)}, 4.8^{c)}$	$\begin{array}{l} 4.8^{\rm b)},1.5^{\rm c)}\\ 7.4^{\rm b)},5.3^{\rm c)}\\ 8.7^{\rm b)},7.8^{\rm c)}\\ 7.8^{\rm b)},6.7^{\rm c)}\end{array}$

^{a)} 1 cd/m², ^{b)}maximum, ^{c)}1 mA/cm².

and a fast time-resolved (15 ps) streak camera (Hamamatsu C4334), was employed to observe the exciton dynamics of the QDs. A transmission electron microscope (TEM, JEOL JEM-2100) was employed to identify the layer thickness in the device. In addition, a depth-profiling XPS (JEOL JPS-903) and ultraviolet photoelectron spectroscopy (UPS, Thermo VG-Scientific, Sigma Probe) were employed to analyze the material composition to deduce the mechanism of positive aging effect.

3. Results and discussion

3.1. Active reagent treatment

Fig. 1(a) shows a cross-section TEM image of the QD-LED configuration. The picture displays four layers on the glass substrate, where the first layer is the ITO anode, the second layer is the organic layer containing HIL and two HTLs, the third layer is the inorganic layer containing QD and ZnO layers, and the last layer is Al cathode. Fig. 1(b) illustrates the energy level diagram of the blue QD-LEDs. The HOMO levels of the organic PEDOT:PSS [24,38], TFB [13] and PVK [24] were 5.2, 5.4 and 5.5 eV, and their LUMO levels were 3.2, 2.3 and 2.0 eV, respectively. The valence bands (VB) of the inorganic QDs (Fig. S1) and ZnO [13] were 5.9 and 7.4 eV, and their conduction bands (CB) were 3.2 and 4.0 eV, respectively. Two energy barriers of 1.4 and 1.3 eV were identified near the QD layer that restrict hole and electron transport and confine the carriers located in the QD layer. Immediately after device fabrication, a bias was applied to the blue QD-LEDs with and without (reference) active reagent treatment. Their EL characteristics, such as L–J–V curves, CE versus J curves, and EL spectra, are presented in Fig. 2. Furthermore, their specific characteristics, such as turn-on voltage (driving voltage at 1 cd/m²), CE_{max} , EQE_{max} , peak wavelength, and fullwidth half-wave maximum (FWHM), are summarized in Table 1. As indicated in Fig. 2(a and b) and Table 1, the reference device demonstrated typical EL performance with a 4.6 V turn-on voltage, a CE_{max} of 0.9 cd/A, and an EQE $_{\rm max}$ of 1.2%. The active reagent device exhibited a more favorable L-J-V, CE, and EQE performance. Therefore, the active reagent reaction may have benefited carrier transport, leading to a





Fig. 3. (a) Transient EL signals of reference and active-reagent QD-LEDs using a driving J of 3 mA/cm². (b) Schematic of the carrier dynamic at the QD/ ETL interface.



Fig. 4. J-V curves of reference and active-reagent QD-EOD (ITO/ZnO/QD/ ZnO/Al). The inset illustrates electron transportation inside the QD-EOD.

considerable decrease in the turn-on voltage from 4.6 V to 3.4 V and a more rapid increase in brightness and CE with the increasing voltage. When J is above 0.9 mA/cm², the active reagent device exhibits higher CE and EQE than those of the reference device, with a CE_{max} of 3.5 cd/A and EQE_{max} of 4.8% for a J of 1.7 mA/cm². Further improvements in efficiency may be obtained when a higher J is used. However, a low operational J was used in this study to prevent device burn down.

3.2. Exciplex or electroplex

Fig. 2(c) illustrates the EL spectra at a driving voltage of 4.4 V. The EL spectral profiles of these two devices appear almost identical, especially in the blue QD emission range with a peak wavelength at 464 nm. However, in the EL spectrum of the reference device, outside the QD emission range, there is a small shoulder ranging from 500 to 800 nm with a peak wavelength near 635 nm, highlighted in the inset of Fig. 2 (c). This side emission may come from the exciplex or electroplex emission at the QD/ZnO interface because an energy difference of 1.9 eV was observed between the ZnO CB and the QD VB. To further investigate, three thin films-QD and ZnO single layers and a QD/ZnO bilaver-were individually deposited on glass substrates for PL measurement, and their normalized PL spectra are displayed in Fig. 2(d). The PL spectrum of the QD/ZnO bilayer was similar to the EL spectrum of the reference device, with a main peak and a small trailing broad shoulder. The main peak profile was identical to the blue QD PL spectrum, with a peak wavelength at 470 nm. However, the broad spectrum in the PL shoulder, ranging from 500 to 700 nm, did not match the shoulder of the EL spectrum (inset of Fig. 2(c)). This PL shoulder represents the ZnO PL emission. No exciplex emissions were detected from the QD/ZnO interface. These findings indicate that the EL shoulder spectrum was the result of electroplex emission. This electroplex emission can be detected when the voltage is applied to the reference device. Electroplex is an energy loss path that degrades device efficiency because partial carriers can be trapped and accumulate at the QD/ZnO interface, thereby generating low-energy electroplex emissions. Stronger electroplex emission corresponded to weaker QD emission because a large number of electrons were trapped at the QD/ZnO interface (approx. 0.8 eV electron-transporting barrier), resulting in low device efficiency. However, the active reagent treatment efficiently suppressed the electroplex emission and increased device performance. These results indicated that the active reagent solution brought the Al atoms into the ZnO layer and formed the alloyed AZO, which raised the CB of the ETL and simultaneously reduced the electron transportation barrier at the QD/ETL interface [27]. Therefore, electron transport at the QD/ETL interface was improved, thus injecting more electrons into the QD layer and generating more blue photons. Therefore, the active reagent device exhibited a lower driving voltage and greater efficiency.

3.3. Carrier and exciton dynamics

The trapped carriers inside the device could be deduced from the TREL signal as illustrated in Fig. 3(a). The TREL signal recorded the delayed emission after turning off the bias, until the signal intensity decayed to 1%. The two devices exhibited similar trends for the TREL delayed emission, which consisted of a prompt decay followed by a delayed signal. The prompt emission resulted from the presence of excitons in the QD layer. The delayed emission resulted from the carriers diffusing and then recombining in the QD layer. The overall delayed emission times were approximately 14.1 and 10.1 µs for reference and active-reagent devices, respectively. These findings indicate that the reference device possessed a larger number of carriers than did the active-reagent device. Furthermore, applying a reverse bias of 7 V after the devices were turned off led to the free carriers and the shallowtrapped carriers being swept out of the QD layer quickly. The TREL signal was used to assess the behaviors of excitons and deep-trapped carriers. The spike of TREL signals near time zero point could be



Fig. 5. (a) PL spectra of reference and active-reagent QD-LEDs, (b) PL spectra of a reference and active-reagent QD-EOD, and (c) TRPL signals of QD thin film, reference and active-reagent QD-LEDs.

deduced the detrapped charge carrier dynamics and recombination because the trapped carriers in the EML and both side interfaces of EML were extracted out when the bias was turned off or reverse [39,40]. Their overall delayed emission times were shortened to 4.7 and 2.7 μ s in the reference and active-reagent devices, respectively. In particular, the active-reagent device exhibited a single prompt decay owing to exciton relaxation. The delayed emission was less easily detected. Dissimilarly, the reference device displayed a large spike signal and a delayed emission, which resulted from a large number of deep-trapped carriers. Therefore, the TREL signals support the idea that the active reagent helps create the alloyed AZO layer, which shifts up the ETL LUMO energy level, reduces the electron injection barrier, benefits the electron into the QD layer to become the shallow trapped charge in the QD layer rather than deep trapped charge (ZnO case) as illustrated in Fig. 3(b).

To clarify the dynamics of electron transport at the QD/ETL interface, two QD-embedded electron-only devices (QD-EODs) were fabricated using the same structure as the ITO/ZnO (21 nm)/QD (18 nm)/ ZnO (21 nm)/Al. One was the reference package and the other was treated with the active reagent solution before encapsulation. A forward bias was applied, and their J–V curves were recorded as illustrated in Fig. 4. The active reagent-treated QD-EOD exhibited a significant improvement in J of one order of magnitude, which was similar to the result for the active-reagent QD-LED depicted in Fig. 2(a) because the alloyed AZO reduced the barrier at the QD/ETL interface and increased electron transport from the ETL into the QD layer, as illustrated in the inset of Fig. 4. Furthermore, electron accumulation at the QD/ETL interface was prevented, thereby suppressing electroplex formation, as



Fig. 6. (a) L–J–V curves, and (b) CE-J and EQE-J curves of active-reagent QD-LED after 0, 97, 409, and 602 h of storage.



Fig. 7. (a) PL spectra of active-reagent QD-LED after 0, 97, 409, and 602 h of storage; J-V curves of (b) reference and active-reagent EOD and (c) reference and active-reagent single-layer ZnO EOD after 0, 161, and 499 h of storage; (d) electroplex emission of reference (409 h) and active-reagent QD-LED after 0, 97, and 409 h of storage.

illustrated in Fig. 2(c). Another possible reason for the improvement in the mobility and conductivity of the ETL seems very minor and it will be subsequently discussed.

The active reagent treatment on the QD layer may partially enhance the efficiency of the active-reagent QD-LED. To investigate this possibility, steady-state PL measurements using an excitation wavelength of 280 nm were made of the QD-LEDs and QD-EODs, with and without the active reagent treatment, as illustrated in Fig. 5(a) and (b), respectively. With active reagent treatment, the QD intensity (peak wavelength, λ_p at 461 nm) was increased in both QD-LED and QD-EOD. The broad background displayed in Fig. 5(b) could be identified as a double-layer ZnO PL spectrum; in Fig. 5(a), several PL spectra from ZnO (λ_p at 401 nm), PVK (λ_p at 414 nm), TFB (λ_p at 435 nm), and PEDOT:PSS (λ_p at 387 nm) were merged. The enhancements of QD peak intensities were $1.64 \times$ and $1.72\times$. The increase in QD PL intensity led to a reduction in the exciton quenching by transforming ZnO to an AZO ETL. When QDs directly contacted ZnO, the interfacial charge transfer induced serious exciton quenching, which has been reported by several groups [41,42]. This interfacial charge transfer could be mitigated in the QD/AZO case. Similar results can be also observed in TRPL measurements on the QD thin film, reference QD-LED and active-reagent QD-LED, as illustrated in Fig. 5(c). The TRPL signal of the reference QD-LED with QD/ZnO exhibited a rapid decay because of exciton quenching. By contrast, the active-reagent QD-LED and original QD thin film both demonstrated almost identical TRPL signal behavior, with a long decay time and reduced exciton quenching. The QD PL enhancements are much smaller than the EQE increase of the reference QD-LED (Fig. 2(b)), suggesting that the efficiency enhancement of the active-reagent QD-LED is in large part attributable to the increase in electron transport because of the ETL active reagent treatment-induced material transformation from ZnO to AZO

3.4. Static positive aging

A second-stage static positive aging process was performed on the active-reagent QD-LED, and the device behaviors versus the various duration of storage times are illustrated in Fig. 6. The device was measured after 0, 97, 409, and 602 h of storage. Fig. 6(a) displays the L–J–V curves, and Fig. 6(b) exhibits the CE–J and EQE–J curves. The EL characteristics are summarized in Table 1. After 97 h of storage, the device exhibited improved EL performance, evident in a reduction in the turn-on voltage and an increase in luminance, corresponding to enhanced efficiency. The emission spectral profiles at various storage times were almost identical to those of the flash active-reagent QD-LED with a peak wavelength of 464 nm and a FWHM of 21 nm (Fig. S2 and Table 1). The optimal storage time was 409 h: at that length of time, the device exhibited the highest relative efficiency with a CE_{max} of 6.2 cd/A and an EQE_{max} of 8.7%. The efficiency was increased by approximately 1.8-fold when the static positive aging matured the device.

To investigate the key factors in the efficiency enhancement of the second-stage static positive aging, analyses of the optical and electrical measurements were performed. Moreover, the PL and EL spectra of the active-reagent QD-LED, and J–V curves of QD-EOD and ZnO-EOD after various storage times were individually recorded, as displayed in Fig. 7. The PL spectra of the active-reagent QD-LED in Fig. 7(a) appear almost identical. Each spectral profile possesses a background shoulder and a main QD emission peak, similar to the spectra presented in Fig. 5. The only minor difference among them was the PL intensity, which exhibited small variations of less than 9% which may reflect slight material recuperation or deterioration of each layer, especially the emissive QD material. Therefore, the contribution of the QD layer appears insufficient to justify the 1.8-fold efficiency enhancement of the QD-LED. The other possible explanation for the efficiency enhancement was that the



Fig. 8. (a) Illustration for sample preparation and material analysis by using UPS and depth-profiling XPS. Depth-profiling (b) Al atom and (c) Zn atom XPS spectra of sample.

ETL transformation led to an increase in electron transport. To investigate this possibility, the J–V curves of the reference and active-reagent QD-EOD were evaluated at 0, 161, and 499 h, as displayed in Fig. 7 (b). The reference EOD displayed slight degradation in J-V performance over time. By contrast, the active-reagent EOD exhibited a significant improvement in J-V behavior. Two possible mechanisms may have led to the improved J-V performance. First, a higher LUMO of the ETL improved electron transport at the interface of QD/ETL. Second, the material transformation of the ETL increased electron mobility. Thus, two single-layer ZnO-EODs with an ITO/ZnO (21 nm)/Al structure were fabricated using two different encapsulations for use as the reference and the active-reagent ZnO-EOD. Their J-V performances after 0, 161, and 499 h of storage were recorded, as illustrated in Fig. 7(c). At first, both devices exhibited closed J-V curves. However, over time, the active-reagent ZnO-EOD exhibited slightly worse J-V behavior compared with the reference one. The reference ZnO-EOD maintained its J-V performance without degradation after 161 h; however, the J-V performance exhibited minor degradation after 499 h. Therefore, it appears that the changes in the electron mobility of the ZnO layer were not a factor during the static positive aging process. Significant electrical improvement with increasing storage time could only be detected in the active-reagent QD-LED and QD-EOD with a QD/ETL interface because the alloying AZO layer reduced the energy barrier of the LUMO and increased the electron transport at the QD/ETL interface, as displayed in Fig. 2(b). The maturing process during static positive aging can be observed by highlighting the electroplex emission spectra (fixing a 3.6 V driving voltage) as displayed in Fig. 7(d). The EL spectral profiles of QD-LED from low to high brightness are almost identical. An electroplex emission spectrum from the reference QD-LED at 409 h was also included in Fig. 7(d). The spectral intensity and profile were similar to those observed at 0 h (inset of Fig. 2(c)). The intensity was fivefold higher than the intensity of the active-reagent QD-LED. By increasing the static storage time, the suppressed electroplex emission of the activereagent OD-LED exhibited lower intensity and a slight blue shift in its spectral profile. The low electroplex intensity was caused by the small energy barrier of the CB at the QD/ETL interface, which supported efficient electron transport, thus preventing the trapping of electrons at the interface and electroplex formation. The blue shifted electroplex emission resulted from the increase of the CB in the ETL, thus increasing the energy gap between the CB of the ETL and the VB of the QD layer for electron-hole pair formation. Therefore, one can conclude that the performance enhancement of QD-LEDs in the positive aging process was principally caused by improved electron transport and reduced exciton quenching as a result of the material transformation of the ETL from ZnO to AZO alloy. The optical behavior of QD is not the factor for the static positive aging process. This ETL transformation can also result in the suppression of the electroplex emission. Currently, the active reagent treatment of acrylic acid does help QD-LEDs to improve the EL performance in the short-term, but its long-term device degradation will be a concern for the practical application and may be solved in the future, which is out of scope of this study.

3.5. ETL transformation

To confirm that the active reagent enabled Al atoms to penetrate into the ZnO nanoparticle layer, a sample was prepared by fabricating a bilayer ZnO (40 nm)/Al (100 nm) thin film and exposing it to an active reagent solution layer on a silicon substrate as illustrated in Fig. 8(a). After a storage time of 336 h, the active reagent was cured and the sample was easily peeled off from the silicon substrate. Depth-profiling XPS and UPS were employed to analyze this sample. In the depthprofiling XPS measurement, the core spectra of Al and Zn atoms were recorded as a function of etching depth from the surface of ZnO layer as shown in Fig. 8(b) and (c). In Fig. 8(b), two growing peaks with increasing depth belong to aluminum oxide (Al-O) and Al- $2p_{3/2}$ at binding energies of ~75.3 and ~72.5 eV, respectively. The gradual increase of Al peak intensities in the depth profile describes the distribution of Al atoms inside the ZnO layer is gradient increase. In particular, 0-nm spectrum shows that Al atoms could be found at the surface of ZnO layer. After 40-nm depth, the core Al spectral area value of the XPS signals become saturated (Fig. S3a), showing the XPS detection has entered into the Al layer. In contrast, with increasing depth, two decreasing peaks belong to $Zn-2p_{1/2}$ and $Zn-2p_{3/2}$ at binding energies of \sim 1046 and \sim 1024 eV, respectively, as shown in Fig. 8(c). Here, a slight peak shift of Zn XPS signals with the increased etched depth was caused from Al diffusion into ZnO layer [30,43]. After 40-nm depth, the core Zn peak intensity of XPS signals become undetectable (Fig. S3b). These depth profile XPS results describe how the proportion of Zn and Al are decreasing and increasing, respectively, while the analysis position moves toward the Al layer. Hence, one can conclude that the active reagent allows the Al atoms to diffuse from the Al layer into the ZnO layer, and even to the ZnO/Si interface. Similar results could be deduced from the UPS results (Fig. S4). Compared to the pure ZnO layer, the UPS spectra showed a shift in energy level during the material transformation from ZnO to AZO.

4. Summarv

The enhanced device performance of blue QD-LEDs was demonstrated using a positive aging process with two steps. The first step, an active reagent was dropped on the cathode surface before device encapsulation, which promoted Al atoms into the ZnO ETL to facilitate electron transport at the QD/ZnO interface, suppressing the electroplex emission and improving the device performances. The electroplex suppression corresponded to a reduction in exciton quenching, resulting from the ETL material transformation from ZnO to AZO, which is also proven by the depth-profiling XPS and UPS analysis. The second step, static positive aging, was then performed by storing the device to enable maturation. After the device matured, the optimal QD-LED exhibited a great efficiency improvement, with a CE_{max} of 6.2 cd/A and an EQE_{max} of 8.7%. When compared to a pristine device without the positive aging process, at a current density of 1 mA/cm², the maximum efficiency enhancement factor was 7.1. In particular, observation of the suppressed electroplex emission revealed that the material transformation of the ETL contributed to the increased electron transport, thereby enhancing device performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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