Stability Study in Cd-free Quantum Dot Light-Emitting Diodes

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ABSTRACT

Although Cd-free quantum dots (QDs) are considered a promising candidate for QD-based light-emitting diodes (QLEDs), poor operational stability should be further improved for their practical utilization in display devices. Here we studied the mechanisms related to the operational stability in Cd-free QLEDs.

1 Introduction

Ever since the first colloidal quantum dots (QDs) were introduced,[1] they have been considered one of the most promising materials in various optoelectronic applications, such as light-emitting didoes (LEDs), photodetectors, and solar cells, owing to their unique and superb properties including wide and intense optical absorption, narrow emission, and band gap tuneability by simply controlling the size of the core.[2–4] In particular, a sharp emission spectrum of QDs, originating mainly from band edges, enables to utilize them for achieving highly color-saturated, wide color gamut (WCG) displays.

One previous huddle for commercialization was that high-photoluminescence (PL) quantum yield (QY) is generally obtained from II–VI QDs containing heavy metal atoms, such as Cd. For example, InP QDs, which are one of the representative heavy-metal-free III–V QDs, typically exhibited lower PL QY than II–VI QDs. As another types of compounds, ternary composition and doped QDs were investigated; however, they show a wide spectral emission (FWHM >50 nm) with broad defect state emission, which deteriorate the advantages of using QDs for WCG displays.

Recently, researchers at Samsung Advanced Institute of Technology have announced huge improvements in InP-based QDs and QLEDs, in terms of efficiency and operational lifetime, which are comparable to those of organic light-emitting diodes (OLEDs).[5,6] Nevertheless, state-of-the-art research results on InP-based QLEDs still far behind to them, particularly in their operational stability. Thus, it is important to study mechanisms related to the stability of InP-based QLEDs, for future QLED displays.

In this work, we investigated the operational stability of the QLEDs consisting of InP-based QDs in the emitting layer, using various measurement techniques, to reveal the degradation mechanism in the QLEDs.

2 Results

We fabricated QLED devices in an inverted device structure,[7] composed of indium-tin-oxide (ITO) as a cathode, ZnMgO (ZMO) nanoparticles as an electron transport layer (ETL), InP/ZnSeS/ZnS QDs in the emitting layer (EML), tris(4-carbazoyl-9-ylphenyl)amine (TCTA) as a hole transport layer (HTL), and MoO_x/Al for an anode. Herein, we inserted a thin insulating layer between ETL/EML or EML/HTL, to make holes and electrons unbalanced under operation on purpose, in order to investigate the effect of excessive carriers on the device stability. As can be expected, both of the charge-unbalanced devices exhibited lower efficiency by a half compared to the pristine QLEDs. However, despite of the lower efficiency, the operational lifetime was measured to be longest in the hole-dominant device, while the electron-rich and pristine devices showed similarly lower lifetime, as shown in Fig. 1.

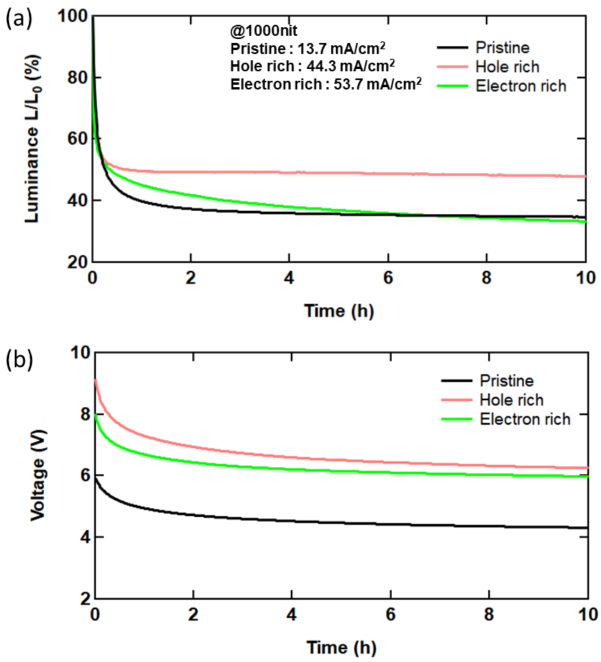

Fig. 1. (a) Relative luminance change and (b) voltage change of InP-based QLEDs in different configurations of the pristine, hole-rich, and electron-rich, measured at an initial brightness of 1000 cd/m^2.

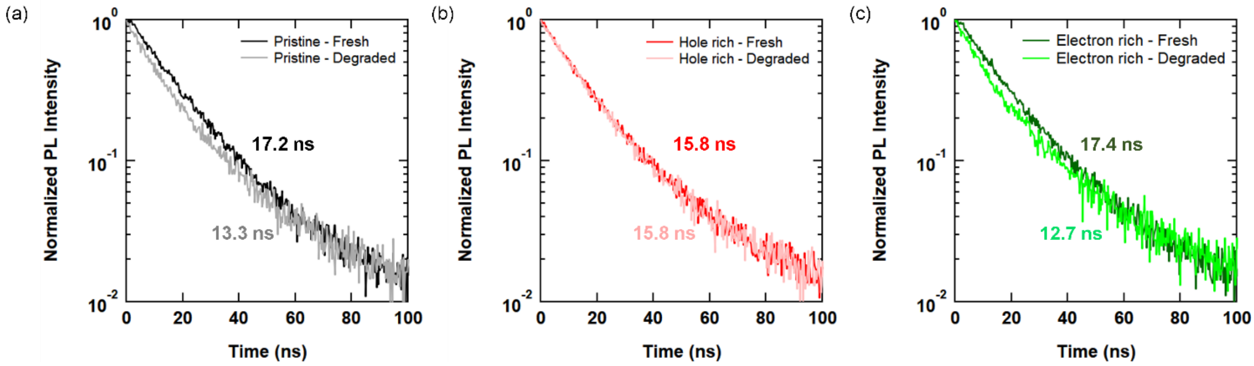

Fig. 2. Comparison of the PL decay time of the QD films in the (a) pristine device, (b) hole-rich device, and (c) electron-rich device, before and after the degradaion.

To reveal the reasons, we adopted several kinds of measurement techniques, such as sing-carrier devices, time-correlated single photon counting (TCSPC), and capacitance–voltage measurement upon degradation. The electron-only devices, in a structure of ITO (150 nm)/ ZMO (30 nm)/QD (20 nm)/ZMO (30 nm)/Al (150 nm), exhibited little driving voltage change (<0.1 V) upon an hour of bias stress at 200 mA/cm^2. However, the hole-only devices, in a structure of ITO (150 nm)/MoO_x (10 nm)/QD (20 nm)/TCTA (50 nm)/MoO_x (10 nm)/Al (150 nm), showed quite a large voltage shift of ~1.5 V at the same bias conditions. We attribute the results to the larger hole injection barrier at the HTL/QD interface compared to the electron injection barrier at the ETL/QD interface. The PL decay time within the devices before and after bias stress was also compared, as shown in Fig. 2. After degradation, the decay time was decreased from 17.2 ns to 13.3 ns. We found that it mainly originated from the quenching near the HTL layer, because only the electron-rich device exhibited similar reduced decay time, as shown in Fig. 2c, but not in the hole-rich device. Therefore, we could say that major exciton quenching sites are formed at the HTL/QD interface and thus, they affect largely to the degradation of the QLEDs.

3 Discussion

Because several factors, such as Auger recombination, Joule heating, degradation of adjacent layers, and defect-induced energy transfer, may affect the degradation of QLEDs simultaneously, we yet cannot fully understand and conclude the degradation of InP-based QLEDs. But we believe that the findings and related mechanisms suggested here will make step forward to develop highly stable QLEDs.

4 Summary

In summary, we investigated device stability of Cd-free, InP-based QLEDs, using a variety of measurement techniques. Based on these experiments, we found that the major degradation occurs from excessive electrons over the device, which can be trapped or charged to quench excitons. We believe that the research results are meaningful for forthcoming application in WCG QLED displays.

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