Developing Cd-free QLEDs for Display Applications

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ABSTRACT

In this study, we investigated the effect of magnesium (Mg) doping in ZnO nanoparticles, in balancing the charge transfer in InP-based QLED devices. Through optimizing QD structures and devices, red InP QLEDs with the current efficiencies as high as 11.6 cd/A were fabricated.

1 INTRODUCTION

Colloidal quantum dot based light-emitting didoes (QLEDs) have earned much attention as the next generation emitter to be used in displays and solid-state lighting due to their highly desirable properties1. Most of the QLED devices in recent years have been fabricated with cadmium (Cd) based II-VI semiconductor QDs. But in recent years the inherent toxicity of cadmium compounds became a big concern, making it critical to search for alternative Cd-free materials. Among possible core materials of Cd-free QDs, indium phosphide (InP) is an excellent candidate due to its wide spectrum range and well-matched energy levels. Unfortunately, both efficiency and lifetime of InP-based QLED devices proved to be much lower compared to Cd-based QLEDs with similar device architecture[2, 3].

In this study, we fabricated red QLED devices with emitting layer formed by Cd-free InP QDs and different electron transport layers utilizing all-solution process. The photoluminescence quantum yield (PLQY) of QD films deposited from the solutions of different concentration had been investigated. Further the effect of different electron transporting layers on electron injection was studied to optimize the electron-hole balance and realize high efficiency in QLED devices. We also investigated the effects of QD emitter PLQY on the QLED device performance.

2 EXPERIMENT

The QLED devices were fabricated through spin coating and evaporation on glass substrates, which were coated with an indium-tin oxide anode.

The substrates were carefully cleaned in deionized water, acetone and ethyl alcohol for 15min each, and then exposed to an UV-ozone cleaner for another 10 min. Hole injection material was first spin coated on the substrate. Then the HI coated substrates were transferred to a N_2-filled glovebox and baked to further remove residual water. After that, HTL layer was then spin coated on the substrates in the glovebox, followed by a thermal anneal treatment. Then green QDs and ZnO nanocrystals were sequentially deposited on the substrates under the same condition and then baked at a certain temperature. The thickness of each layer can be adjusted by changing the solution concentrations and spin speeds. After the deposition of the solution-processed layers, all samples were transferred to a vacuum deposition chamber with chamber pressure less than 10−6 torr ($P < 10^{-6}$ torr) for Al cathode (100 nm thick) deposition, followed by the final encapsulation with a UV-curable epoxy and cover glasses in the N_2 glove-box. All the devices had the emitting area of 2 mm^2 that was defined by the overlapping of ITO and Al electrodes.

The optical and electrical characteristics of QLEDs were taken under ambient conditions by a spectro-radiometer (Minolta CS 1000) and the experimental set-up with a Keithley 2400 source meter and a silicon photodiode.

3 RESULTS

A schematic device structure and an energy band diagram of the Cd-free QLEDs are shown in Figure 1. In the device, the PEDOT:PSS and TFB are used as hole injection and transport layers respectively, and $Zn_{1-x}Mg_xO$ nanoparticles with different dopant ratio (x = 0, 0.05 and 0.15) are used as ETL.[4] The energy band structure of the cadmium-free QLED devices is shown in Figure 1b. Due to the fast electron injection into InP QD layer through the ZnO ETL, the imbalance between hole and electron currents within the device happens. Doping ZnO with Mg results into band gap broadening and energy level shift with the increase of Mg concentration, producing a larger energy barrier between an Al cathode and ZnMgO ETL, effectively reducing electron injection.

Here, core-shell InP/ZnSe QDs are used as an emitting material in R-QLED devices. These RQDs show the PL peak at 621 nm, FWHM of 54 nm and PLQY of 35%.

To test the effectiveness of electron current density reduction in QLED devices with raised Mg doping ratio in ZnMgO ETL on QLED performance we fabricated a series of QLED devices with the following structures: ITO/PEDOT:PSS/TFB/InP-RQD/ZnO/Al (ZnO+Al), ITO/PEDOT:PSS/TFB/InP-RQD/$Zn_{0.95}Mg_{0.05}O$ /Al (ZMO (a) +Al), and ITO/PEDOT:PSS/TFB/ InP-RQD/$Zn_{0.85}Mg_{0.15}O$ /Al (ZMO (b) +Al).

Electroluminescence performance of these devices is summarized in Figure 2. Looking at current density and brightness of the devices (Figure 2 (a)), two trends can be observed–with the increase of Mg doping concentration in ZnMgO ETL current density is decreased, while brightness is increased.

By controlling Mg doping concentration in ZnMgO ETL we were able to achieve an almost 3-fold efficiency improvement – from 1.2 cd/A with ZnO ETL to 3.0 cd/A with $Zn_{0.85}Mg_{0.15}O$ ETL.

Despite the pronounced effect of balanced charge injection having on the electro-luminescent display device efficiency, it is still impossible to achieve very high efficiency when QLED devices utilize QD emitters with low PLQY.

Recently we were able to synthesize a sample of InP RQDs, and these RQDs exhibited a much higher PLQY compared to those with InP/ZnSe core/shell structure (60% vs. 35%). In order to compare device performances, QLEDs with the following compositions had been fabricated: ITO/PEDOT:PSS/TFB/InP-RQD(35%)/$Zn_{0.85}Mg_{0.15}O$/Ag, and ITO/PEDOT:PSS/TFB/ InP-RQD(60%)/$Zn_{0.85}Mg_{0.15}O$/Ag. The results of IVL measurements are summarized in Figure 3. There is a significant difference in brightness (Figure 3 (a)), resulting into almost one order of magnitude increase in brightness when 60% PLQY emitter is utilized. The improved luminescence of the RQDs also results into much higher efficiency – it increased from 3.0 cd/A for 35% PLQY to 11.6 cd/A for 60% PLQY.

This is a promising result, suggesting that more efforts being spent on researching and developing new InP-based QDs now, when CdSe-based QDs toxicity has become an important issue urging people toward Cd-free QDs, a significant improvement in InP-based QLED performance is possible with increase in high PLQY InP QDs availability.

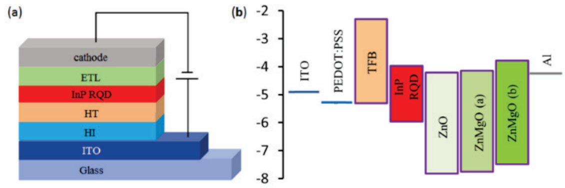

Fig. 1 a) Basic device structure of InP QLED with ITO anode; b) Energy band diagrams of InP QLEDs with ZnO, $Zn_{0.95}Mg_{0.05}O$ (a), and $Zn_{0.85}Mg_{0.15}O$ (b) ETLs

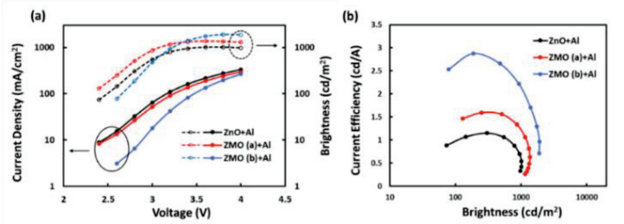

Fig. 2 Current efficiency of the InP R-QLED devices utilizing ZnO, $Zn_{0.95}Mg_{0.05}O$, and $Zn_{0.85}Mg_{0.15}O$ ETLs

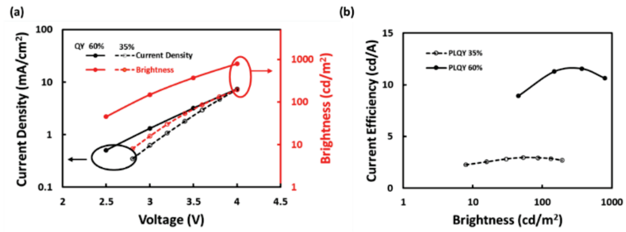

Fig. 3 Characteristics of QLED devices, utilizing InP-based RQDs with 35% and 60% PLQY: (a) Current density and brightness; (b) Current efficiency.

4 DISCUSSION

We reported a study of the factors responsible for InP-based R-QLED device performance. We showed that electron current density in these devices is generally much higher than hole current density, resulting into unbalanced charge injection. By controlling band gap, mobility and electron injection barriers of ZnMgO ETLs through changing Mg doping concentration we were able to achieve much more balanced charge injection resulting into nearly 3-fold efficiency improvement. It has been also shown that current state of InP QD development for QLED applications is still far behind that of CdSe QDs. We demonstrated that improving PLQY of InP QD emitters in conjunction with balanced device structure can result into significant efficiency improvement.

CONCLUSIONS

By increasing InP RQD PLQY from 35% to 60% we were able to achieve a very high efficiency of

11.6 cd/A for InP based R-QLED devices. We also showed that top-emitting architecture of InP based R-QLED devices can lead to significant reduction of FWHM compared to bottom-emitting architecture (from 54 nm to 32 nm), resulting into much higher color purity, which is very important for use of this materials in display applications.

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