Investigation Ink-jet Printed Quantum-dot Light-emitting Diodes Lifetime Properties by IPL Post-treatment of ZnO NPs Electron Transport Layer

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ABSTRACT

By applying intense-pulsed light (IPL) post-treatment to zinc-oxide nanoparticles (ZnO NPs) to stabilize the hole-electron injection within the quantum-dot emission layer (QD EML) of ink-jet printed quantum-dot light-emitting diodes (QLEDs), the device lifetime properties have been remarkably improved.

1 INTRODUCTION

High color purity, stability based on inorganic material properties, and emission wavelength control by size adjustment are some of the key advantages that show that QD is an attractive option as a strong candidate for next-generation displays. [1–3]

Ink-jet printing is mainly in the spotlight as a QLEDs manufacturing method for commercialization in the industry, and studies on this suggest various possibilities for applying ink-jet printed QLEDs to actual product manufacturing. [4, 5]

ZnO is a material used as an electron transport layer for QLEDs, and various studies have been conducted. Since remarkable research has already been conducted in the field of thin film transistors, [6, 7] it is showing a fairly rapid progress in being used as an ETL of QLEDs. [8, 9] Conventional structure In the case of QLEDs, since ETL is formed on the QD EML, high-temperature processes above 100 degrees are not allowed. This is because the QD and underlying layers (hole injection layer (HIL) and hole transport layer (HTL)) can be deteriorated by heat energy. As such, in the case of ZnO applied to the QLEDs field, ZnO NPs thin film is formed by a solution process mainly by dispersing ZnO NPs in a solvent. Due to the difference in these process methods, it is necessary to have a different approach from conventional bulk ZnO deposition.

ZnO is an oxide semiconductor with strong n-type characteristics based on oxygen vacancy [10, 11], and is very suitable as an ETL of QLEDs. However, oxygen vacancy can also lead to drawbacks that cause scattering during trap formation and electron transfer in ZnO. These phenomena can adversely affect the electrical stability of QLEDs and should be eliminated.

In this study, we propose IPL post-treatment to stabilize the time dependency of ink-jet printed QLEDs by rapidly removing oxygen vacancy in ZnO NPs ETL. IPL process effectively minimizes the deterioration of the lower layers because the process is completed in a short time, and studies on this prove that IPL is an effective post-treatment method [12] . The stabilization of device characteristics without deterioration was proven by the current-voltage-luminance (IVL) characteristics analysis of the fabricated ink-jet printed QLED.

2 EXPERIMENT

ITO coated Glass substrate were sonicated with acetone and IPA for 1 hour each, followed by UV ozone treatment for 20 minutes. Poly(3,4-ethylenedioxy-thiophene) : poly(styrenesulfonate) (PEDOT: PSS, Clevios P VP AI 4083, Heraeus Co., Germany) used as HIL was mixed with IPA at a ratio of 1:1 and sonicated for 5 minutes, spin-coated at 2000 revolutions per minute (rpm) for 30 seconds, and then annealed on a hot plate for 100 °C for 30 minutes. Poly [9, 9-dioctylfluorene-co-N-(4-(3-methyl-propyl)) diphenylamine] (TFB, OSM Co., Korea) used as HTL dispersed in toluene at a concentration of 8 mg / ml was stirred at 50°C at 400 rpm for one day, spin-coated at 4000 rpm for 30 seconds, and then annealed at 150°C for 30 minutes on a hot plate. QD (In-visible Co., Korea) of CdZnSeS core / ZnS shell structure was dispersed in a solvent mixed with hexane and oDCB 1:2 at a concentration of 20 mg / ml, and then steered at 400 rpm for 2 hours at room temperature (RT). QD EML was formed by ink-jet printing and then annealed on a hot plate at 100 °C for 30 minutes. The ZnO NPs ETL was formed by ink-jet printing using N-11 purchased from AVANTAMA (Switzerland) and then annealed on a hot plate for 60 °C 30 minutes. Annealing and ink-jet printing process were performed in a dinitrogen (N_2) atmosphere glove box except for spin-coating process performed in an air atmosphere. After the solution process, aluminum (Al) used as cathode was deposited at 2 Å / sec to 100 nm thickness by thermal evaporator under high vacuum pressure of 2×10-7 Torr. Finally, after thermal evaporation, the QLEDs fabricated with Glass / ITO / PEDOT: PSS / TFB / QD / ZnO / Al structured was encapsulated in N_2 atmosphere glove box.

3 RESULTS

Fig. 1 shows the flow chart of the ink-jet printed QLEDs manufactured in this study and the images of photoluminescence (PL) and electroluminescence (EL) of ink-jet printed QLEDs. QD ink and ZnO NPs ink have an orthogonal solvent relationship, and dissolving or intermixing at the interface between TFB HTL and QD EML is prevented by optimizing the TFB thin film [ ]. PL and EL photographs of ink-jet printed QLEDs show uniform and accurate ink-jet printing of QD ink and ZnO NPs ink within the 80 ppi (60 μm × 240 μm) pixel.

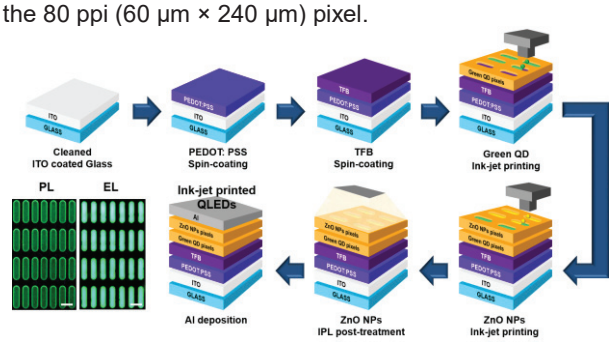

Fig. 1 Schematics for ink-jet printed QLEDs Fabrication and images of PL and EL of ink-jet printed QLEDs

We applied the IPL post-treatment conditions in which the oxygen in the IPL chamber fills the oxygen vacancies of the ZnO wurtzite structure by the light and heat energy from the xenon lamp, and **Fig. 2a** and **b** illustrate the conceptual diagram of this experiment. The transmittance of ZnO has a property that the transmittance increases as the metallicity or oxygen vacancies decrease [13] , and this experiment achieved an increase in transmittance due to the reduction of oxygen vacancies in the ZnO NPs thin film by IPL post-treatment aimed at reducing oxygen vacancies. This is shown in **Fig. 2c**. The image of Inset shows the process schematic and process conditions of the post-IPL processing.

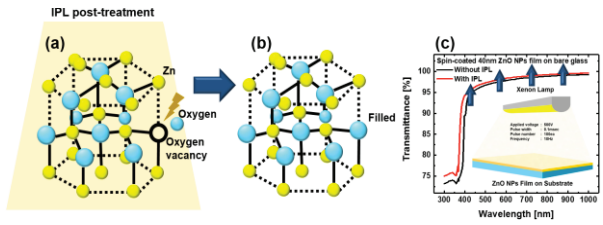

Fig. 2 Oxygen vacancies in wurtzite structured ZnO are filled with oxygen by IPL post-treatment, and the decrease in defect density due to reduction of oxygen vacancies in the ZnO thin film increases the transmittance of ZnO thin film. (ZnO thickness: 40nm)

The effect of the oxygen vacancies in ZnO being filled by IPL post-treatment on the electrical and optical properties of ink-jet printed QLEDs was investigated. From immediately after the device encapsulation was completed to the 8th day, the current density, luminance, current efficiency, and EQE of ink-jet printed QLEDs were compared and analyzed according to the presence or absence of IPL post-treatment on ZnO ETL. In the case of ink-jet printed QLEDs without IPL post-treatment, the current density gradually decreases over time, and the current efficiency and EQE characteristics are stabilized from the 6th day (**Fig. 3a**, **b**, and **c**). The gradual increase in efficiency characteristics appears to be due to a phenomenon in which the balance of hole-electron injection in the QD EML improves as the oxygen vacancy in the ZnO ETL decreases. On the other hand, in the case of QLEDs using ZnO NPs ETL that has undergone IPL post-treatment, the decrease in current density is relatively small compared to QLEDs without IPL post-treatment, and current efficiency and EQE are stabilized from the after 2 day (**Fig. 3a**, **b**, and **c**).. By IPL post-treatment, the oxygen vacancy in the ZnO NPs ETL is filled with oxygen, and the hole-electron injection balance in the QD EML is achieved early compared to the QLEDs without IPL post-treatment process. The slight decrease in efficiency characteristics is due to light energy damage to the QD EML during IPL post-treatment. This can be minimized by optimizing the process conditions of IPL post-treatment.

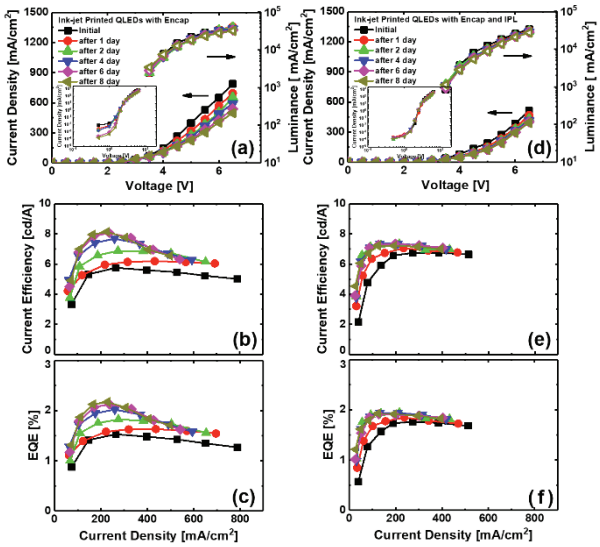

Fig. 3 Stabilization of the IVL characteristics of ink-jet printed QLEDs by IPL post-treatment

The effect of the improved hole-electron injection balance on the lifetime characteristics of ink-jet printed QLEDs is shown in **Fig. 4**. **Fig 4a** and **b** depict hole-electron recombination and excitation in QD EML due to the effect of oxygen vacancy reduced by IPL post-treatment. If the IPL post-treatment was not applied, it may cause a decrease in performance and a decrease in lifetime due to electron accumulation due to a relatively

large amount of electrons. The L_T/L_0 value that rapidly decreases from the initial state of the lifetime curve in **Fig. 4c** to about 7 hours proves this phenomenon. Over time, the decrease in electron injection as oxygen vacancy is filled increases the L_T/L_0 value again, and the general lifetime curve is displayed again from about 35 hours. In the case of IPL post-treatment was applied QLEDs, the amount of charge in the ZnO NPs ETL decreases as shown in **Fig. 4b**, and the accumulation of electrons is prevented, and a general life curve is displayed as in **Fig. 4d**. The lifetime of the improved ink-jet printed QLEDs was measured to be about 28 hours and 5 minutes.

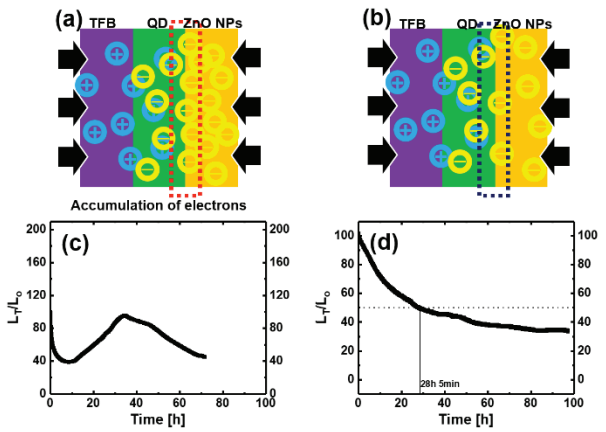

Fig. 4 Improvement of ink-jet printed QLEDs lifetime property by matched hole-electron injection balance due to the IPL post-treatment

4 CONCLUSIONS

In this study, by controlling the amount of charge in ZnO NPs by IPL post-treatment, the time-dependency of QLEDs was improved, thereby improving the IVL characteristics and lifetime characteristics of QLEDs. The performance of encapsulated QLEDs did not decrease even without IPL post-treatment, and this contributed to dramatically showing the effect of IPL post-treatment. The IPL post-treatment effectively filled the oxygen vacancies in ZnO with oxygen, and the transmittance measurement of the ZnO NPs thin film proved this. The time taken to stabilize the time dependence of QLEDs by IPL post-treatment has been drastically reduced from 6 days to 2 days. Based on this results, it was confirmed that electron accumulation at the interface between QD EML and ZnO NPs ETL is prevented by IPL post-treatment, thereby improving the lifetime characteristics of QLEDs. In order to control the characteristics of ZnO NPs used as ETL of QLEDs, IPL post-treatment requires only a short time and a simple process, which will help to fabrication of the better performance QLEDs.

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