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Water repellent spray-type encapsulation of quantum dot light-emitting diodes using super-hydrophobic self-assembled nanoparticles

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ABSTRACT

We have developed a spray-type encapsulation method for quantum dot light-emitting diode (QD-LED) displays designed to prevent the penetration of oxygen and moisture in ambient air and repel water. The non-wettability and oxygen/moisture repellency afforded by the super-hydrophobic (contact angle of ~158°) self-assembled Al_2O_3 nanoparticles (SAM-NP) is attributed to a reduction in the number of defects sites such as pin-holes or cracks during the formation of the thin-film. The QD-LEDs with SAM-NP encapsulation were found to have an effective lifetime in ambient air and a stable light emission in water compared to those of equivalent QD-LEDs without encapsulation.

1. Introduction

There has been active interest in the development of quantum dot light-emitting diodes (QD-LEDs) and organic LEDs (OLEDs) as these can provide a greater purity and reproducibility of color than conventional LED and plasma display panel (PDP) displays, as well as being better suited to flexible and/or transparent applications [1–5]. However, there is a downside to these QD-LED and OLED materials in that their luminescent lifetime rapidly deteriorates when exposed to ambient air. Indeed, QD-LED and OLED materials are well known to be very weak in oxygen and moisture rich environments [6–8], and are therefore currently encapsulated in glass with a moisture absorber when used in commercial and research-scale QD-LED and active matrix OLED devices. This use of solid glass, however, prevents their use in flexible and/or transparent display devices, and so in order to overcome this important issue, various thin-film encapsulation methods have been introduced: (i) Al_2O_3-thin-film encapsulation by atomic layer deposition (ALD) [9], (ii) polymer film encapsulation with poly-*p*-xylylene and/or poly-2-chloro-*p*-xylylene [10], (iii) encapsulation with epoxy resin such as ERL-4221, Eporite-5630 or D.E.R.-331. [11], (iv) multi-layer-based encapsulation with AlO_x and plasma polymer films [12], (v) silicone encapsulation [13], (vi) thin-film-based encapsulation with heat-stabilized PET, SiO_2-barrier film, or a SiN_x-capping layer [14], and (vii) encapsulation with ZrO_2/epoxy nano-composite [15].

Although numerous encapsulation methods have been developed, the formation of cracks and pin-holes remains an issue that needs to be resolved at any cost as these degrade the effective light time of display devices. Moreover, when thin film encapsulation materials based on inorganic, organic, or inorganic/organic multi-layers are directly exposed to water, the display lifetime is further deteriorated by the penetration of water molecules. Thin-film encapsulation by vacuum deposition and spin-coating methods also limits the use of thin-film passivation materials, as these cannot be applied to flexible, concave/convex, or uneven substrates due to their complex structure. A roll-to-roll process for OLED displays has been recently developed for the fabrication of large-scale displays, but only ALD and ALD/polymer hybrid encapsulation processes have been investigated. However, this ALD process is not only expensive, but also requires a relatively long tack time when compared to spin-coat and spray processes. This in turn has a direct bearing on the production cost, which is obviously a very important consideration in commercial display devices. There is therefore clearly a need to develop a novel spray-type passivation method that can not only be easily and cheaply applied to substrates with a complex structure, but can also perfectly protect display materials

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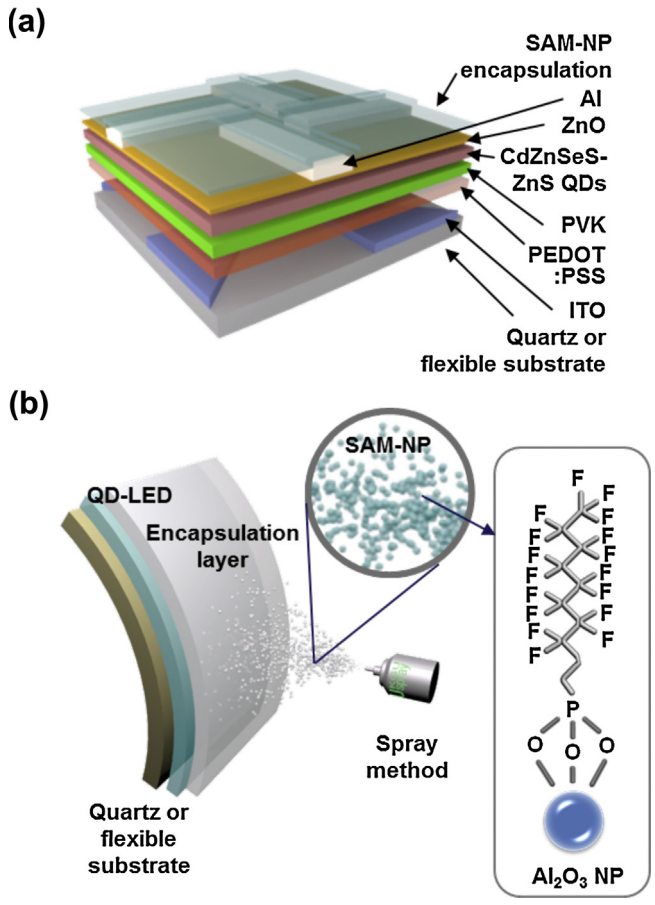

Fig. 1. (a) Schematic diagram of an all-solution-processed QD-LED device based on a ITO/PEDOT:PSS/PVK/CdZnSeS-ZnS QDs/ZnO NP/Al structure. (b) Schematic showing the encapsulation of a QD-LED substrate in a SAM-NP solution via a spray coating method.

from oxygen and moisture in ambient air and from direct contact with water.

In this study, we investigate the luminance and effective lifetime of QD-LEDs before and after applying a heptadecafluorodecphosphonic acid (HDF-PA) based spray-type encapsulation solution. This fabrication method and the encapsulation properties of the HDF-PA based solution are described in detail, and their hydrophobicity in water and oxygen/moisture repellency in ambient air is assessed in comparison to QD-LEDs without encapsulation. The effective lifetime of QD-LEDs without encapsulation, with Al_2O_3 nanoparticles (NP) encapsulation, and with HDF-PA self-assembled Al_2O_3 NP (SAM-NP) encapsulation are also evaluated in ambient air, and the stability of QD-LEDs in water is also evaluated.

2. Experimental

A schematic depicting QD-LEDs with a passivation layer of SAM-NP is shown in Fig. 1a. To create the QD-LED, an indium tin oxide (ITO) thin film 100 nm in thickness was first deposited by radio frequency sputtering system to provide an anode, which was then spin-coated with poly (ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) to a thickness of 20 nm (3000 rpm for 60 s) to produce a hole injection layer (HIL). A 20-nm-thick hole transport layer (HTL) was then applied by spin coating a poly(N-vinylcarbazole) (PVK) solution (0.05 g PVK in 5 ml of chlorobenzene) at 3000 rpm for 60 s. Next, a CdZnSeS/ZnS quantum dot (~45 nm) light emitting layer (EML) was coated at 2000 rpm for 20 s, followed by a 40-nm-thick electron transport layer (ETL) formed by spin coating a 25–30 mg/ml ZnO NP–ethanol solution at 1500 rpm for 60 s. Note that after deposition of the HIL, HTL, EML, and ETL layers the substrate was annealed at 150, 150, 60, and 60 °C, respectively. Finally, a thin (100 nm) film of Al was deposited by direct current sputtering to provide a cathode.

A SAM-NP encapsulation layer was applied to the QD-LED substrate by airbrushing (DH-103, Spamax) a HDF-PA solution (Apollo scientific Ltd, UK) containing self-assembled Al_2O_3 NPs (diameter of 20 nm, Sigma Aldrich, USA) (Fig. 1b). To prepare this solution, 80 g of Al_2O_3 NPs was first mixed with HDF-PA (5 mM) in a semiconductor-grade isopropyl alcohol solution (100 mL), and then sonicated for 1 hour to induce self-assembly. The injection velocity and amount of spray were controlled by varying the flow rate of N_2 gas (0.2 MPa), as well as the distance between the spray nozzle and the substrate (~10 cm), such that a 3 min deposition time equated to a layer thickness of 2 μm.

The electroluminescent characteristics of the fabricated QD-LEDs without encapsulation, with NP encapsulation, and with SAM-NP encapsulation were measured using a Konica-Minolta CS-1000 spectroradiometer coupled with a Keithley 2400 DC power source. The life-times of the devices were all measured at constant current of 3 mA, and their stability in water was examined at time intervals of 5 min (between 0–60 min) or 10 min (between 60–120 min) at a constant voltage of 4 V. The oxygen and water vapor permeability of the SAM-NP encapsulation (device size of $5 \times 5 \times 0.1$ cm^3) was characterized by permeability analysis (MOCON, USA OX-TRAN Model 2/21 and PERMATRAN-W MODEL 3/33, respectively). The oxygen and water vapor permeability were measured at 23 °C and 37.8 °C with 100% RH (relative humidity), respectively.

3. Results and discussion

A representative example of the bright green emission from the 3×3 mm active region of a QD-LED on a plastic substrate with SAM-NP passivation is shown in Fig. 2a. The surface morphology of the SAM-NP thin-film is shown in the top right of this FE-SEM image, and reveals a uniform coverage over the QD-LED layers. The photo-image in the bottom right shows the super-hydrophobic nature of this SAM-NP-coated substrate, with its contact angle being more than 158°. Fig. 2b shows the representative luminescence and current density characteristics of green-emitting QD-LED devices without encapsulation, with NP encapsulation, and with SAM-NP encapsulation. The turn-on voltage of luminance was ~3 V in all cases, but variation was seen in the maximum luminance of the emissive area; with ~8,077 cd/m^2 at 9 V, ~9,579 cd/m^2 at 11 V, ~9,940 cd/m^2 at 10 V in the non-encapsulated, NP encapsulated and SAM-NP encapsulated QD-LEDs, respectively. The variation in current density as a function of applied voltage exhibited an unconventional linear behavior with a slope of 67.7 mA cm^{-2} V^{-1}, 99.0 mA cm^{-2} V^{-1}, and 118.6 mA cm^{-2} V^{-1} in the non-encapsulated, NP encapsulated and SAM-NP encapsulated QD-LEDs, respectively; indicating the formation of Ohmic contacts between the anode/cathode and HIL/ETL layers, respectively. Fig. 2c shows the current efficiency versus voltage for the three QD-LED types, with the current efficiency reaching an average maximum of around 21.9 cd/A at 7 V, 18.0 cd/A at 9.5 V, and 19.3 cd/A at 10 V with non-encapsulation, NP encapsulation and SAM-NP encapsulation, respectively. These results indicate that encapsulation with NP or SAM-NP does not reduce the luminance, current density or current efficiency of QD-LED devices.

Fig. 3 shows the normalized luminance versus relative lifetime for non-encapsulated, NP encapsulated and SAM-NP encapsulated QD-LEDs operated at 3 mA. Note that the effective lifetime of the QD-LEDs was defined in this study as the required for