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Patterned mist deposition of tri-colour CdSe/ZnS quantum dot films toward RGB LED devices

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In this experiment a technique of mist deposition was explored as a way to form patterned ultra-thin-films of CdSe/ZnS core/shell nanocrystalline quantum dots using colloidal solutions. The objective of this study was to investigate the feasibility of mist deposition as a patterning method for creating multicolour quantum dot light emitting diodes. Mist deposition was used to create three rows of quantum dot light emitting diodes on a single device with each row having a separate colour. The colours chosen were red, green and yellow with corresponding peak wavelengths of 620 nm, 558 nm, and 587 nm. The results obtained from this experiment show that it is possible to create multicolour devices on a single substrate. The peak brightnesses obtained in this experiment for the red, green, and yellow were 508 cd/m, 507 cd/m, and 665 cd/m, respectively. The similar LED brightness is important in display technologies using colloidal quantum dots in a precursor solution to ensure one colour does not dominate the emitted spectrum. Results obtained in-terms of brightness were superior to those achieved with inkjet deposition. This study has shown that mist deposition is a viable method for patterned deposition applied to quantum dot light emitting diode display technologies.

Keywords: colloidal quantum dots, nanocrystals, mist deposition, patterning, light emitting diodes.

1. Introduction

The display industry continues to search for low energy, high brightness, high colour purity and flexible displays. In recent years the advancement in synthesizing colloidal quantum dots (QDs) has led to the progression of applications that could meet the needs for the next generation of displays. QD light emitting diodes (QD-LEDs) have since been developed to electrically inject electron-carriers and hole-carriers into a layer of colloidal semiconductor quantum dots to produce light emission. The QD-LEDs are solution processible by virtue of the multilayer device configuration that is similar to polymer light emitting diodes (OLEDS) [1–3]. Through the use of inorganic semiconductor nanodots rather than organic compounds for light emission the long term reliability and stability under varied ambient conditions could potentially increase.

The present study is concerned with the development of QD-LED based display technology using colloidal solution precursors. Specifically, it focuses on the formation of three-colour matrices, which can then be applied to the fabrication of the display. Creating a three-colour display requires a deposition technique that offers pattern-ability in a selected area, without damaging the previously deposited colour layers, and the ability to replicate small patterns.

Among techniques available for the purpose of QD thin film deposition using colloidal solution, spin-coating techniques cannot be used here because it does not allow patterned deposition. An alternative approach, spray pyrolysis requires the medium to be sprayed at the surface at moderate to high temperatures to induce evaporation. The high temperature process could cause damages to the underlying hole-transport-layers (HTL) in the devices. The spray pyrolysis also uses high speed particles that will splash upon surface contact, which is undesirable for smooth films [4,5].

Another patterning method is the inkjet printing process which uses QDs in nonpolar solvents as an ink [6]. A common problem associated with inkjet print technology is the creation of microstructures as the solvent evaporates due to mass transport, which often leads to gaps and voids causing pin-hole defects [8]. Another limitation is that the printer heads often clog and create empty spaces where ink should have been deposited, which in-turn also creates pin-hole defects [8,9]. Additionally, the process creates uneven surface roughness that reduces the overall performance of the devices [8,9].

In this study the technique of mist deposition was chosen because it allows for pattern-ability in a selected area, without damaging the previously deposited colour layers and the ability to replicate small patterns. It has been shown that the mist deposition process can create patterns on the substrate surface and that it is possible to pattern separate coloured CdSe/ZnS core/shell QDs (purchased from Ocean

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Nano Tech) without damaging any previously deposited QD layer [10,11]. The ability to replicate a pattern accurately will prove necessary when patterning three separate colours closely together. Mist deposition can be used to create patterned depositions of multiple colours in the micron range without damage to other existing layers [10,11]. The mist deposition process has been used for other LED applications already such as blue OLED technology, and proven its ability to create high brightness LEDs [12]. It was also successfully used to deposit ultra-thin QDs of QDs, which is crucial for QD-LEDs since brightness of the QD layer exhibits a critical dependence on film thickness [13–15].

2. Experiment

The device structure utilized in this study for the multicolour QD-LED array is the same structure used in a single colour QD-LED [14,15]. Figure 1 depicts the composition of the device stack that was used in this experiment with respective layer thicknesses. For device processing, first, indium-tin-oxide (ITO) stripes running the length of the glass substrate were patterned through lithography and wet chemical etching. Next, a 30-nm-thick layer of poly(3,4--ethylene dioxythiophene) doped with poly(styrenesulfonate) was deposited onto the glass via spin coating and annealing. The next layer is the ~45 nm HTL of poly(N,N'--bis (4-butylphenyl)-N,N'-bis(phenyl)benzidine), deposited via spin coating and curing again.

The surface of HTL is then patterned with the CdSe/ZnS core/shell QD layer of the desired colours using the mist deposition process. Mist deposition is a technique that utilizes an atomizer to create small droplets of a carrier solution that carries the desired medium to the substrate [10]. The QDs are first put into a colloidal toluene solution to ensure even distribution in the liquid carrier. Nitrogen is then fed through the carrier solution to create a mist that is carried to the atomizer via nitrogen pressure at a flow rate of 1 ml/min. The atomizer then uses inertial separation to select the properly sized droplets, which means larger droplets will not follow the nitrogen flow but rather collide with the sidewalls. The atomizer outputs droplets that are approximately 0.25 microns in size which are then driven towards the surface using an 8-kV electric field. The droplets will pass through a mask and contact the surface of the sample in a pattern that matches the mask that is being used. Figure 2 shows a schematic of the mist deposition tool, including the deposition chamber, the atomizer and the toluene bubbler.

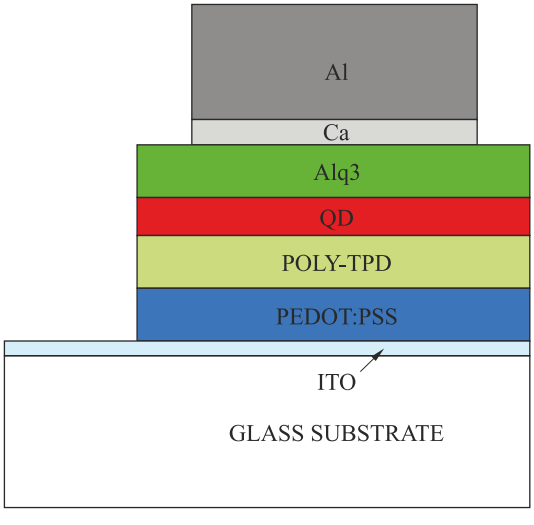

Fig. 1. The device structure used in the QD-LEDs.

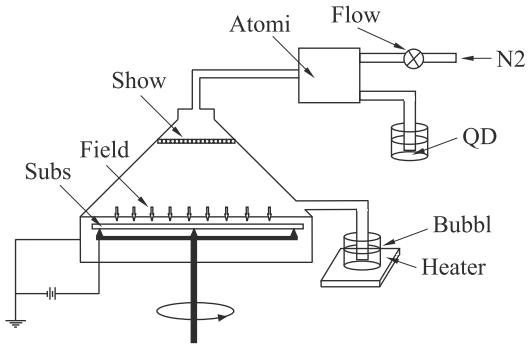

Fig. 2. A schematic drawing of the mist deposition tool. Shown here is the atomizer, bubbler, chamber, and rotating stage.

In the present study, the toluene bubbler heats toluene to 50°C and decreases the evaporation rate of the toluene on the substrate surface. The mist flow rate is 1 ml/min for 20 minutes keeping the voltage at 8 kV with the bubbler heated to 50°C, which creates a layer that is roughly 1–5 monolayers and cured at 80°C for 30 minutes. The 30-nm electron transport layer, tris-(8-hydroxyquinoline) aluminium (Alq3 purchased from American Dye Source) is then added via thermal evaporation under a pressure of 3×10^{-7}. Finally, the top electrode of Ca/Al (~10 nm/~150 nm) is deposited via thermal evaporation [1].

Figure 3 depicts the masking and deposition process used to create the three-color devices. To create the three--color displays, the surface is covered except for a thin strip that matches an indium-tin-oxide (ITO) strip underneath. The first colour QDs are then deposited on the selected ITO strip [Fig. 3(a)]. It is crucial that the deposited QD strip matches the width of the ITO or is slightly wider. If the QD layer does not cover the entire ITO stripe, then the uncovered portion will cause recombination in the Alq3 layer or the poly-TPD layer which is undesirable. Following deposition the atomizer and tool are cleaned to remove any trace of the initial QDs. The process is then repeated two more times with two remaining ITO strips to create a three-color QD--LED matrix [Fig. 3(b)] [10]. Finally, the top electrode is deposited onto the devices using thermal evaporation [Fig. 3(c)].

The light-current-voltage characteristic of the QD-LEDs was measured using a Keithley 4200 semiconductor parameter analyser, in conjunction with a Newport 818-SL silicon detector and a 1830-C Newport optical power meter. The matrix was then passively addressed using an National

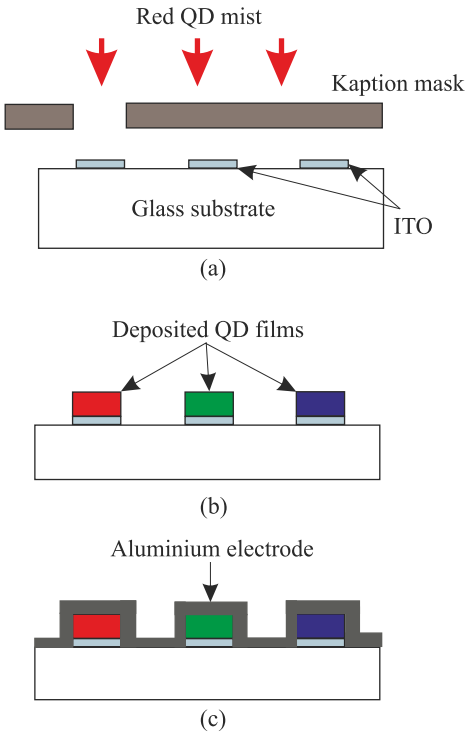

Fig. 3. A simplified version of the QD-LED fabrication using mist deposition. (a) The deposition of the first QD layer through a mask. (b) The three-color device after the three QDlayers are deposited onto the surface of the substrate. (c) The top electrode is then deposited onto the surface via thermal deposition to create a QD-LED where the Al and ITO cross.

Instrument PXI-2536 switching matrix, which enables the first pixel in the first row to be turned on then off followed by the second pixel being turned on and off. The switching cycle rasters through all the pixels illuminating them one at a time and then repeats at the beginning again with a speed of 1000 Hz. The matrix was passively addressed at 14 V and illuminated under a continuous 14 V, and both methods showed promising results.

3. Results and discussion

As mentioned earlier the goal of this study was to create a passively driven three-colour display. Figure 4 shows the result of the three-colour QD mist deposition. In this figure, the three colours are evenly spaced and all have a similar brightness. The pixels are about 2 mm by 2 mm in size. This size was chosen for the ease of manual alignment of the masks. The pixels are illuminated using the passive display method with a driving voltage of 14 V and a scan speed of 100 Hz. The minor defects seen in Fig. 4 on the surface are believed to be related to non-uniformities in the spin-coated poly-TPD layer underneath the QD region (Fig. 1), which in turn is related to the initial cleanliness of the glass substrates. Clean substrates used in large area devices are important because the smallest particle can create ripples in the spin coating which will then be increased in each layer that is added afterwards. Mist deposition is capable of creating conformal coatings [Fig. 6(b)] over the pre-existing layers on the device. If the layers deposited via spin coating have any ripples from spin coating, the mist deposited film will replicate the same structure which is observed in Fig. 4. The emission colours also vary slightly for some pixels depending on the Alq3 emission. There are some pixels that have a slight Alq3 emission in the green regime that slightly changes the tint of the QD-LED towards the green regime.

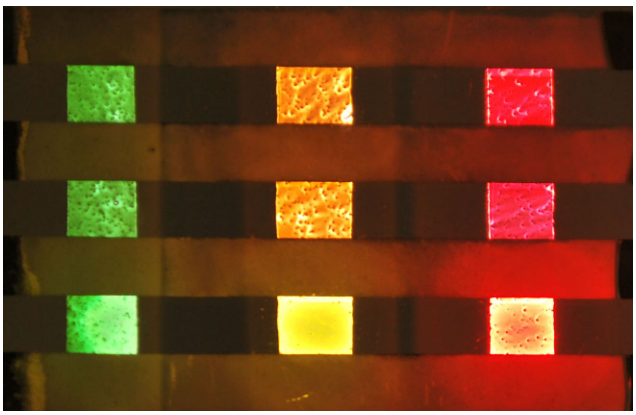

Fig. 4. A three by three passively driven matrix consisting of green, yellow, and red QDs. The surface defects indicate ripples in the poly-TPD layer and slight changes in color are due to changes in the Alq3/poly-TPD emission.

In the next part of the study, the device performance of the deposited films was investigated. Figure 5(a) shows the brightness of the mist deposited quantum dot arrays. The inset inside of Fig. 5(a) shows the current-voltage characteristics of the devices which were all similar and peaked at 2.5 A/cm^2 which is constrained by the measuring circuit. The peak brightness for all three devices differed by 32% compared to inkjet deposition which has a 188% difference [15]. The peak brightness for the red is 508 cd/m^2 (620 nm), the yellow brightness peaks at 665 cd/m^2 (587 nm), and the green peaks at 507 cd/m^2 (558 nm). Each device has a separate peak brightness which is related to the efficiency of the individual pixels. It should be noted that the devices were powered with a voltage corresponding to 14 V rather than peak brightness voltage, 22–25 V, to prevent heat degradation. While powered at 14 V the brightness of red was 58 cd/m^2, the yellow brightness was 57 cd/m^2, and the green brightness was 73 cd/m^2, which means the values differed by 28% at the driving voltage making them appear equivalent in brightness. In the next part of the experiment, the intensity *vs.* the wavelength of the emitted radiation was investigated, Fig. 5 (b) shows the normalized intensity and spectra of the three-colour QD--LEDs which all exhibit narrow-band spectra. The peak emission for the red QDs is centred at 620 nm, the yellow peak emission is at 587 nm, and the green peak emission is at 558 nm, which match the emission wavelengths by design. The green QD emission spectrum shown in Fig. 5(b) was obtained after subtracting the emission line originating from the Alq3 layer (Fig. 1). The normalized inten-

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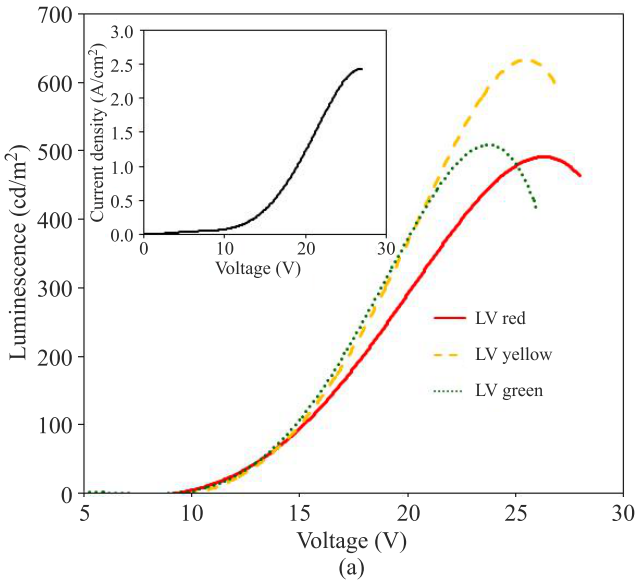


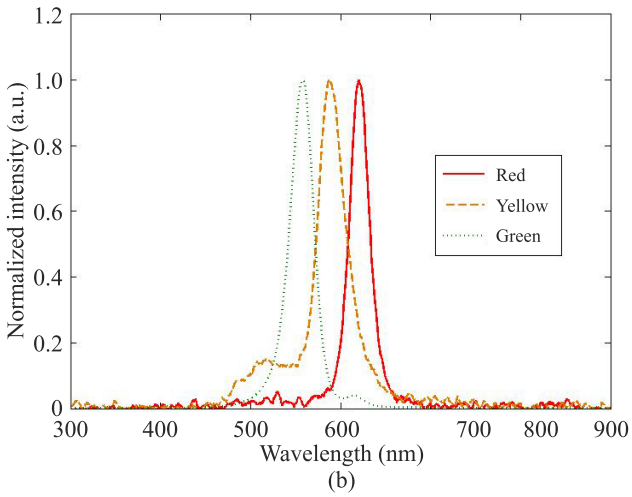
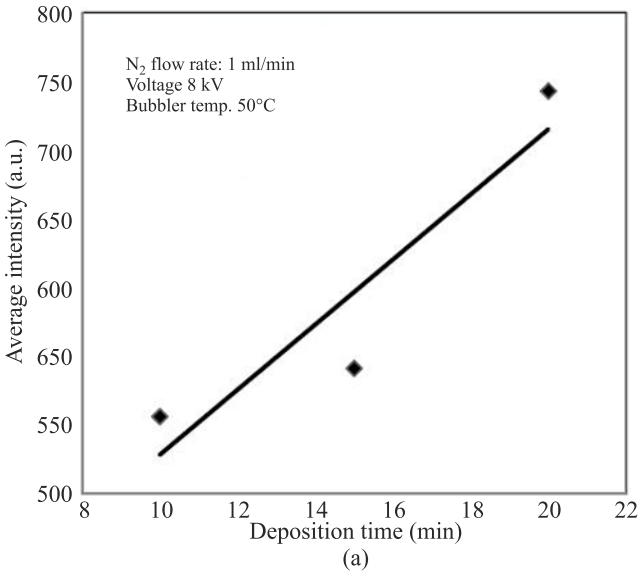


Fig. 5. (a) Plot of the luminescence vs. the voltage. For each QD-LED color the luminescence increases to peak brightness before heat starts to affect the luminescence. The inset shows the current density vs. the voltage which is representative for all 3 devices. (b) The normalized intensity vs. wavelength plot for each QD-LED color. The green peak had the Alq3 emission subtracted since it was close to the green QD emission. The emission from each QD-LED matches the expected emission provided by the manufacturer (Ocean Nano Tech).



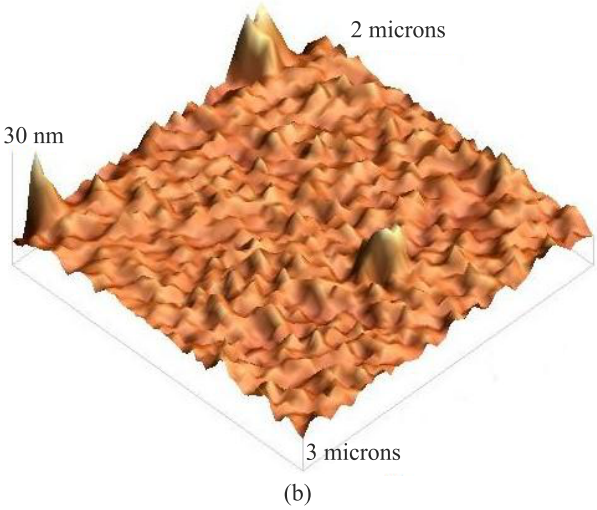


Fig. 6. (a) The average intensity vs. deposition time. The longer the deposition time the greater the average intensity. This plot demonstrates the linear dependence of average intensity and deposition time. (b) An AFM scan of green QDs deposited onto a glass substrate using the set parameters (1 ml/min flow rate, 8 kV electric field, and 50°C bubbler temp). The resulting RMS roughness of the film is 2.5 nm.

sities show a weak Alq3 emission in the yellow peak which could indicate the QD layer is too thin.

The thickness of the QD film is crucial to the LED performance, because the thickness dictates the maximum brightness of the emission from the active region. Furthermore, since the electron-mobility and the hole-mobility are different in the electron and hole transport layers (Fig. 1), a proper design in the QD thickness helps to ensure the electrons and holes recombine in the QD layer rather than a transport layer. The film thickness is dependent on the flow rate and the deposition time. In Fig. 6(a), the change of the QD film intensity as a function of time is shown. As the plot in this figure demonstrates the intensity increase has a linear dependence, where intensity correlates to thickness of the deposited QD layer. The mist deposition process has control over thickness as well as the ability to create smooth films.

Studies have shown that the extent of surface roughness of QD films also has a significant impact on the performance of the resulting LED [16,17]. Figure 6(b) shows an atomic-force-microscopy (AFM) scan of the mist deposited QD layer. The film that was analysed was formed under the same conditions as the actual devices under study. The mechanically coherent film uniformly coats the surface with a root mean square (RMS) roughness of 2.5 nm. The smooth surface is free of pits and peaks that could create pinhole defects in the device.

4. Conclusions

The purpose of this study was to show that it is possible to create a multicolour QD-LED array on a single substrate using mist deposition and passively address it. The results obtained indicate that it is possible to create a multicolour QD-LED array on a single substrate. Through the use of mist deposition it is possible to pattern separate colours onto a single device. The mist deposition process creates smooth surfaces that allow for high brightnesses from the QD--LEDs. The QD-LEDs are capable of reaching brightnesses of 665 cd/m^2 and still have room for further improvement. The emissions of the QD-LEDs match the emission wavelengths that the manufacturer provided. The results of the study prove that it is feasible to create a multicolour RGB array using QD-LEDs through the use of mist deposition.

Acknowledgements

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