High-quality Quantum-Dot-Based Full-Color Display Technology by Pulsed Spray Method

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ABSTRACT

We fabricated the colloidal quantum-dot light-emitting diodes (QDLEDs) with the HfO_2/SiO_2-distributed Bragg reflector (DBR) structure using a pulsed spray coating method. Moreover, pixelated RGB arrays, 2-in. wafer-scale white light emission, and an integrated small footprint white light device were demonstrated. The experimental results showed that the intensity of red, blue, and green (RGB) emissions exhibited considerable enhancement because of the high reflectivity in the UV region by the DBR structure, which subsequently increased the use in the UV optical pumping of RGB QDs. In this experiment, a pulsed spray coating method was crucial in providing uniform RGB layers, and the polydimethylsiloxane (PDMS) film was used as the interface layer between each RGB color to avoid cross-contamination and self-assembly of QDs. Furthermore, the chromaticity coordinates of QDLEDs with the DBR structure remained constant under various pumping powers in the large area sample, whereas a larger shift toward high color temperatures was observed in the integrated device. The resulting color gamut of the proposed QDLEDs covered an area 1.2 times larger than that of the NTSC standard, which is favorable for the next generation of high-quality display technology.

Keywords: Light-emitting diodes, Quantum dots.

1. INTRODUCTION

Recently, great efforts have been made to develop colloidal quantum dot (CQD) light-emitting technologies into display application. The benefits primarily depend upon QD's narrow bandwidths, high luminescence efficiency, broad absorption, and tunable band gaps[1-3]. However, several issues associated with CQDs are hindering their wide application of the commercial products. Most of recent studies focused on promotion of quantum efficiency of these nano-scale particls, or various techniques to render better white LEDs such as co-doping QDs in phosphor, crosslink of colloidal QD layer etc [4-6]. In addition to these progresses, how to combine QD layers into device structure is another task. Spin mist coating and inkjet printing have been proposed and demonstrated [7-9]. However, these methods all suffer from their own shortcomings. For spin mist coating method, the loss of QD solution is high and the cross-contamination in red-green-blue (RGB) pixels can be detrimental [10]. Meanwhile, the inkjet printing method caused the non-uniform surface and inaccurate diameter definition [11]. How to separate the individual RGB pattering and keep the uniformity of RGB color are crucial for industrial application.

In this study, the fabrication of QDLEDs including pixelated arrays and full-wafer light source are demonstrated, and the individual RGB QD layer is sprayed by pulse spray coating method. The polydimethylsiloxane (PDMS) is employed as the interface to separate the individual CQD layers. Furthermore, a highly reflective HFO_2/SiO_2 distributed bragg reflector (DBR) is employed to increase the utilization of UV light in RGB QDs. As the results, the QDLEDs with highly reflective DBR could provide enhancement in individual RGB colors and white light emission.

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The optical properties of three QD products purchased from Sigma-Aldrich® were first characterized using UV-visible absorption and photoluminescence (PL) spectroscopy. As shown in Fig. 1, both red and blue QDs exhibited an absorption edge that is consistent with the bulk band gap energy of CdSe (Eg = 1.7 eV) and CdS (Eg = 2.5 eV). This result was consistent with that of X-ray diffraction (XRD) analysis, in which the observed diffraction peaks were identified as wurtzite CdSe and cubic CdS. For QDs that emit green, an absorption onset located between the band gap energy of ZnS (Eg=3.7 eV) and CdSe was observed, indicating the existence of an alloyed structure of $Cd_{1-x}Zn_xSe_{1-y}S_y$. The corresponding XRD pattern showed the diffraction behavior of wurtzite ZnS, with an apparent shift of the main peak caused by alloying with CdSe.

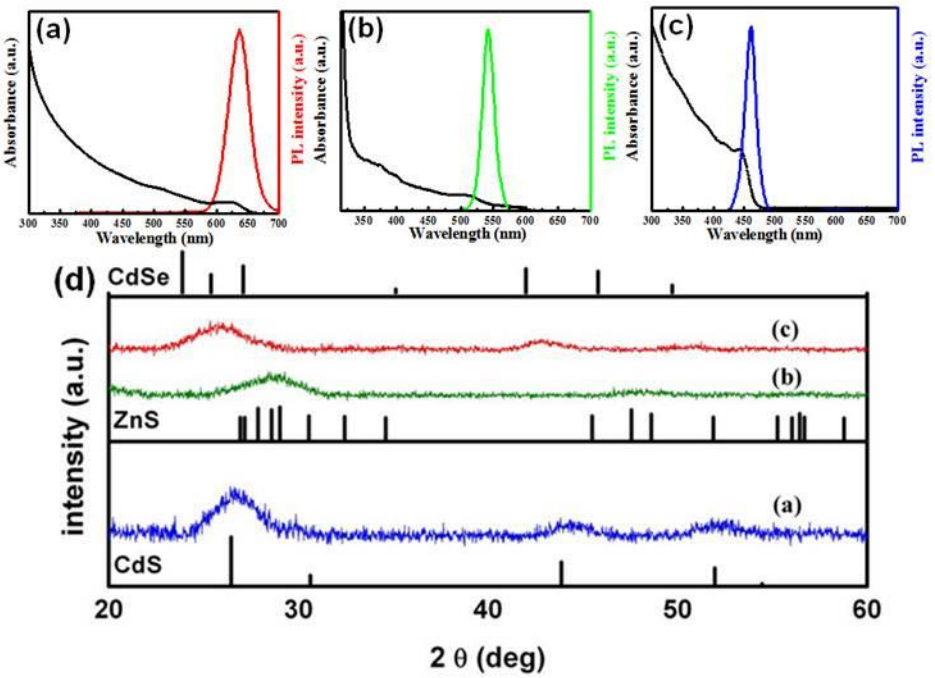

Figure 1. UV-visible absorption and PL emission spectra of QDs with the emission colors of (a) red, (b) green, and (c) blue; the corresponding XRD patterns are shown in (d). In (d), the reference patterns of wurtzite CdSe (JCPDS 77-0021), wurtzite ZnS (JCPDS 72-0163), and cubic CdS (JCPDS 65-2887) are also included for comparison.

2. EXPERIMENT

The pulsed spray (PS) coating method was used to spray the RGB QD layers [12]. In traditional spraying techniques, the viscosity of the spraying mixtures can considerably affect the uniformity of the finished film. The interaction between the particles in the premixed solution can cause a gathering of the materials, and self-clustering can block the passage of the spray. The PS method can improve this issue using two special designs, that is, using the air-injection mechanism in the nozzle and intermittent spraying frequency (5 to 10Hz), and using the constant stirring system. These methods can separate the target particles in the suspending solution more effectively than traditional methods. Thus, the atomized mixture of quantum dots and solvent can pass through a tiny nozzle to reach the desired surface, further reducing the chances of quantum-dot self-assembly. The actual operation was precisely controlled by a computer network, and the quantity of the spray can be monitored.

Figure 2 shows the process flowcharts of the pixelated RGB QD arrays and non-patterned white light source on a 2-in. substrate. The concentrations of the RGB QD were approximately 1 mg/ml. The pixelated arrays shown in Fig. 2 were fabricated using the following steps: 1) an 11-pair HfO_2/SiO_2 DBR was evaporated in an ion-assisted e-gun system on the top of the glass; 2) the mask was placed on the top of the substrate for alignment; and 3) the RGB QDs were sprayed onto the surface of the glass in the sequence of green, blue, and red. Similar steps can be followed for a 2-in. wafer white light source; however, no mask alignment is used.

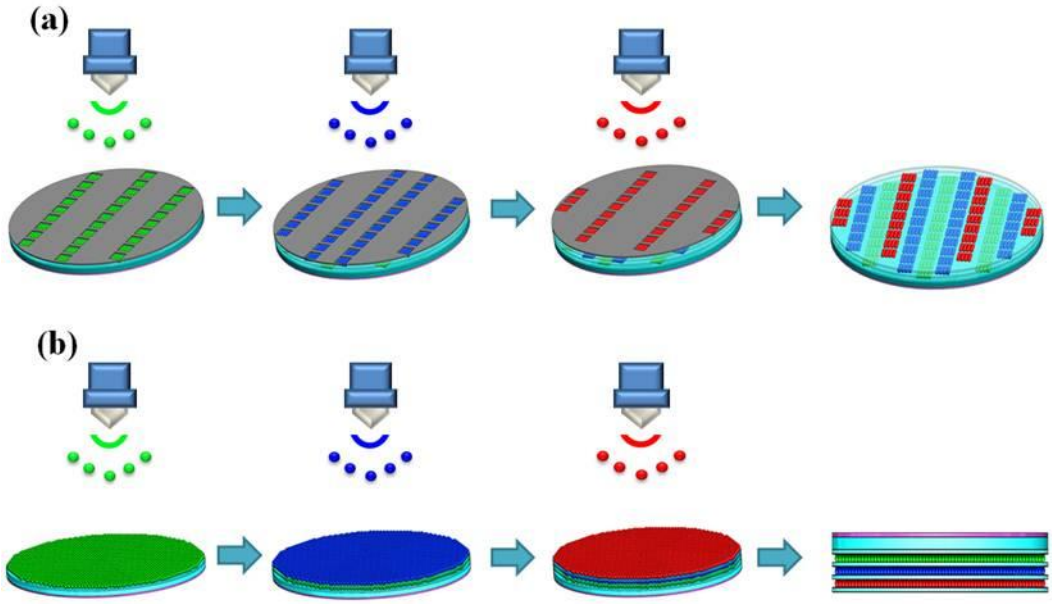

Figure 2. Schematic illustration of (a) pixelated arrays (b) full-color by pulsed spray coating method.

3. RESULTS AND DISCUSSION

A simple large area sample was first fabricated to verify our idea. Multiple layers of PDMS film were made separately, and deposition of CQDs was performed between PDMS stacking layers. As described in the Experimental section, an 11-pair HfO_2/SiO_2 DBR thin-film structure was placed on top of the sample. In the DBR structure, the maximal reflectivity was designed for a UV wavelength of approximately 400 nm, and the refractive index of the HfO_2 and SiO_2 layers were 1.9 and 1.46, respectively. Over 90% of reflectivity can be maintained between 365 nm and 430 nm; the wavelength of the UV source was 380 nm. By contrast, the reflectivity was lower in the visible spectral range. The mirror stack was designed to enable SiO_2/HfO_2 DBR to reflect most of the UV light and transmit the visible photons. Therefore, the reflected UV photons excited more RGB QDs and increased the efficiency of pumping.

Fig. 3(a) shows the relative intensity of the large-area samples with DBR under a driving current of 350 mA in a UV pumping LED, compared with the reference without DBR. The result demonstrates that the large-area samples with DBR have higher intensity in red, blue, and green components than the reference without DBR. The reflection of light from the DBR structure can enhance the efficiency because the increased light path leads to a higher possibility of exciting the RGB QDs. The CIE color coordinates of the large-area samples with DBR, which provide a white light output, are (0.29, 0.29) shown in the inset of Fig. 3(a). To further verify the pumping power dependence of each color, the driving current of the UV LED was varied from 100 mA to 400 mA. The enhancement of each color from the DBR sample over the non-DBR sample is shown in Fig. 3(b). A saturation of this enhancement ratio was observed among red, green, and blue QD emissions beyond 250 mA, which indicates a possible quench in the quantum yield of the quantum dots. Additionally, the enhancement ratio of red emission was higher than that of the other colors, which can be attributed to

the proximity of red QD layers to the UV source. Although the transparency in PDMS is high, slight UV light loss occurs in each PDMS layer. However, PDMS performs a crucial role in separating the RGB QDs in our structure, and can further isolate the air from RGB QDs, which can stop the intensity degradation in RGB QDs. The green QDs exhibited a weaker enhancement in general. This may have been caused by the substantial aggregation of green QDs when they were sprayed and dried on the substrate. This phenomenon indicates that green QDs experienced considerable aggregation during the solidification process, which is the main cause for the lower enhancement ratio observed for the LED. Further information can be acquired from the absorption spectrum. A smaller absorption of the green dot was observed from the direct measurement of reflection and transmission on solidified quantum dots on glass (Table I), which also indicates a possible decrease in UV excitation efficiency.

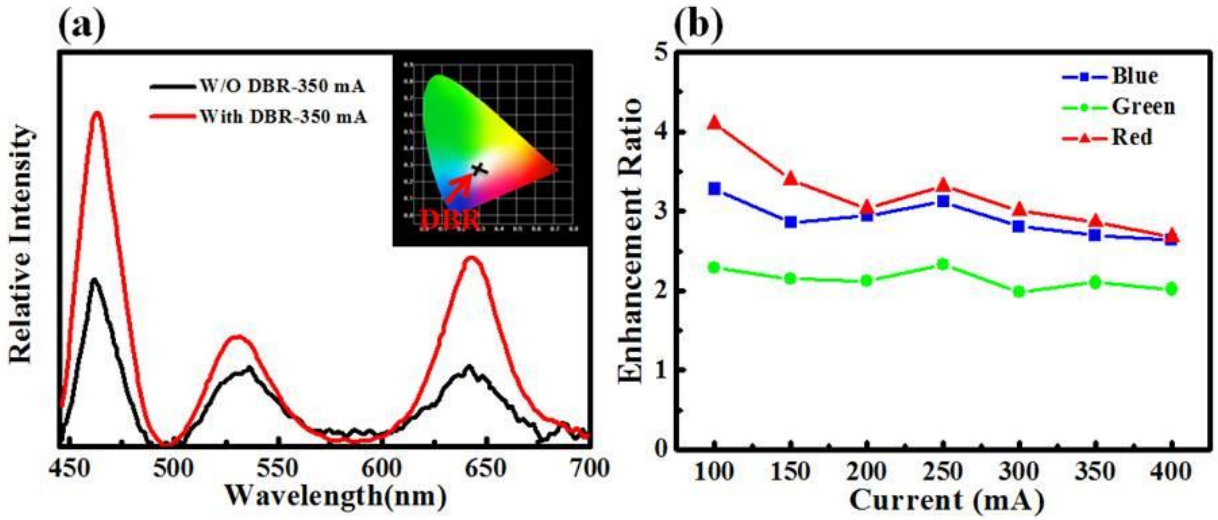

Figure 3. (a) The relative intensity of the large-area samples with and without DBR operated under 350 mA. The inset shows the CIE color coordinates of the large-area samples with DBR. (b) Enhancement ratio of the intensity of large-area samples with and without DBR under various currents from 100 to 400 mA.

The chromaticity coordinate of the large-area samples with DBR remained almost the same with the increase of the driving current, which indicates that the large-area sample with the DBR structure has high stability in color rendering, and this characteristic is crucial in solid-state lighting. With this pump-power-independent color mixing, our PDMS-layered structure can provide a tunable color-rendering scheme by adjusting the quantities of the RGB QDs of each layer. Additionally, the CIE coordinates of the large-area samples with DBR were compared to the National Television System Committee (NTSC) standard color triangle. The RGB color coordinates for the large-area samples with DBR were (0.69, 0.3), (0.19, 0.75), and (0.13, 0.05). Therefore, the area of the RGB triangle of the large-area samples with DBR was enhanced by 20%, compared to the NTSC color gamut. This result can be attributed mainly to the narrow bandwidth in the RGB QDs, which have high color purities.

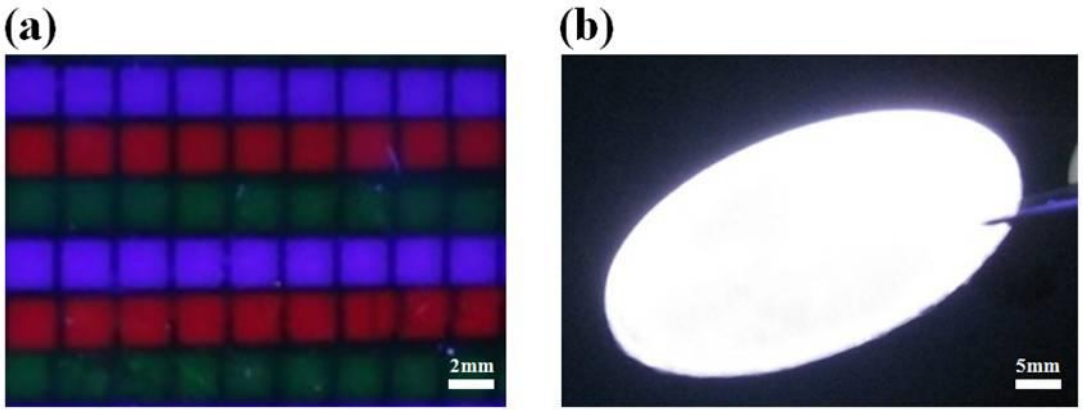

Figure 3. Image of the (a) pixel pattern, (b) a 2-in. full wafer structure under UV excitation.

After finishing the large area test, we further shrank the scale to an actual LED package. Fig. 4(a) shows the schematic diagram of QDLED and a picture of a real QDLED in operation. Fig. 4(b) shows the electroluminescence (EL) spectra of our QDLED with and without the DBR structure. The background of pure UV LED emission is also shown in the figure. Three emission peaks occurred at 460 nm (blue band), 530 nm (green band), and 640 nm (red band), which were contributed by the RGB QDs. This indicated that EL with the DBR has stronger visible emission than that without the DBR structure.

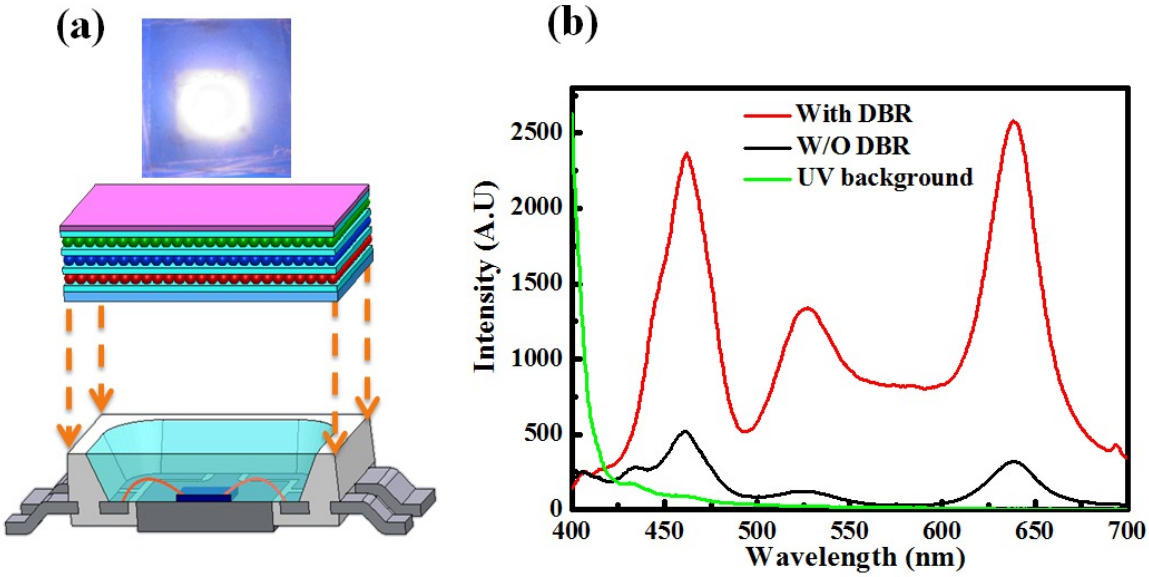

Figure 4. (a) top: the QDLED device in action; bottom: the device schematic diagram. (b) EL spectra with and without the DBR structure.

4. CONCLUSION

In conclusion, this study demonstrated an integrated platform of colloidal quantum dots, UV LEDs, PDMS multiple layers, and DBR stacks that can achieve enhanced performance of full-color white light emission. Both large area and micron scale integrated devices were demonstrated. With the addition of UV DBR stacks, the use of pumping UV photons can be enhanced, which increases the output power of RGB. Furthermore, the chromaticity coordinates of the large-area samples with DBRs remained pump-power-independent, whereas those of the integrated device exhibited a larger shift under elevated pumping power because of possible thermal issues. Finally, QDLEDs with the DBR structure fabricated using the pulsed spray coating method demonstrated an excellent optical characteristic with high stability, which can provide an alternative approach in display technology.

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