Ink-Jet Printing and Photolithography of Quantum Dot Patterns for Micro Light-Emitting Diodes

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ABSTRACT

Two types of quantum dots (QD) patterning methods applied in micro-LED color conversion process are studied in this article. QDs were patterned by ink-jet printing and by photolithography to from QD array with pitch/size of 40/20 μm respectively, and were further excited by a blue LED for luminescent property measurement. QD ink-jet printing pattern shows red light emission peak of 626 nm and a FWHM of 38 nm. Compare to ink-jet printing method, QD photolithography pattern shows the emission peak with longer wavelength of 635 nm and a broadened FWHM of 43 nm.

1 Introduction

Micro- light-emitting diodes (micro-LED) have attracted significant interest due to their advantage of small size, high brightness, high contrast and high efficiency. These advantages make micro-LED display become a promising candidate of AR/VR display [1]. However, to achieve a full-color display is still challenging. Two major methods are currently considered: self-emissive RGB pixels and color-converted RGB pixels. In the self-emissive pixels, each color component in a pixel is formed by a micro LED chip. So for a full-color pixel, we have at least 3 different types of semiconductor LEDs to be put together. While this method provides the best efficiency and a very good color quality, it needs to be noted that the difficulties to make all these different types of devices onto the same substrate or panel. Another concern rises from the reduction of the quantum efficiency of the LEDs when their sizes are reduced [2, 3] and proper passivation is needed to slow down this decrease in quantum efficiencies. On the other hand, the color-converted pixels require only a monochromatic micro LED array, and the other colors (usually red and green) can be provided by the color conversion layer (CCL) which can transform the high energy photons into the lower ones, and be made of colloidal quantum dots (CQDs) [4-6]. Thus the difficulty in the fabrication of the micro-LED side is greatly reduced. But instead, we need to master the procedure to pattern these color conversion materials into arrays of small pixels. Although there are many choices on the CCL, we will focus more on the colloidal quantum dots in this study. To pattern color conversion material on micro scale LED requires accurate control of pattern size and alignment. Ink-jet printing and photolithography are two distinguished choices for small pattern sizes, both of them can reach pattern size smaller than 5 μm in this study.

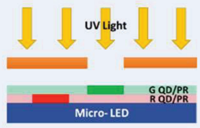
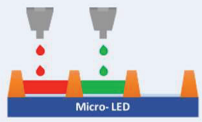
Method	Photolithography	Ink-jet Printing
		
Pros	□ High throughput □ High uniformity □ Scattering particles	□ Lower QD cost □ Less QD damage □ Easy to repair QD pattern
Cons	■ Unfriendly process to QD (UV exposure & alkaline developer) ■ Higher QD waste	■ Low throughput ■ Resolution and alignment challenge ■ Higher requirement of ink dispersion ■ Uniformity and Interface issue

Table. 1 Advantages and disadvantages of QD photolithography and QD ink-jet printing process

QD photolithography process has the benefits of high throughput and high uniformity of pattern. However, the UV exposure and alkaline developer during the process could be harmful to the quantum dots. Another concern is that the high percentage of the QD material will be washed away after the photolithography processes, and thus we waste plenty of the active material. QD ink-jet printing on the other hand, shows the benefits of low material cost and preserve most of the QD quality. Still, it faces the challenges of throughput and pattern uniformity caused by interface issue. The comparison of QD photolithography process and QD ink-jet printing process is shown in Table 1.

In this paper, 20 μm QD pattern array were formed via ink-jet printing process and photolithography process respectively. Their luminescent properties were investigated with a blue LED excitement of 450 nm emitting wavelength. The QD photoluminescence spectrum were collected and discussed in details. We hope this comparative study can provide further information for the future improvement of the full-color micro-display fabrication.

2 Experiment

Quantum dots with size and pitch of 20/40 μm were patterned by both ink-jet printing method and photolithography method on the same type of glass substrate with black matrix. Black matrix was patterned by gray photoresist through photolithography process with line width of 20 μm and thickness of 6 μm. The QD loaded samples were then excited by a blue LED light source with emitting wavelength of 450 nm and measured by a 2D spectroradiometer for their optical properties.

2.1 QD Ink-jet printing

Ink-jet printing on micro-LEDs requires small droplet size down to micrometer scale. The ink-jet printer we used is made by SIJTechnology, Inc.. Different from other printers like those using piezo-electric effect or thermal bubble, this printer by SIJ uses a novel type of electro-hydrodynamic technique [7]. Its droplets volume is able to as small as 1 fL (1 femtoliter = 10^{-15} liter), and reach the drop size diameter to micro-meter scale. However, with the smaller droplet, the ink-jet nozzle diameter need to reduce to 1.5- 5 μm, which becomes a challenge to QD ink material dispersion. QD ink require high dispersibility for avoid aggregation on the nozzle tip.

For 20 μm QD pattern, we chose nozzle with 5 μm diameter for printing. QD ink was dispersed in UV monomers with 30 wt%. Under the control of voltage, frequency and printing speed, red and green QD can print smoothly with dot size and line width near 20 μm as shown in Fig 1. Other test patterns such as parallel lines are also shown to verify the uniformity of the spraying process.

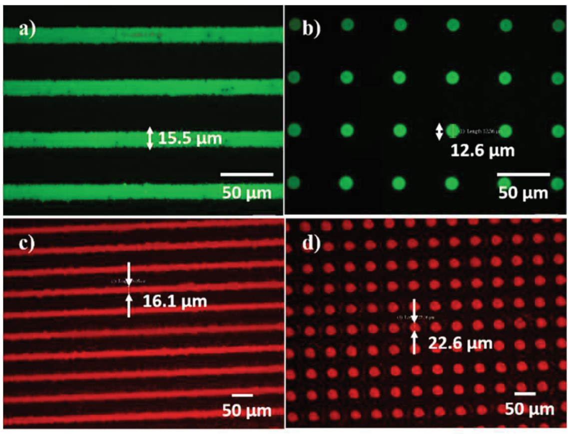


Fig. 1 Fluorescence optical microscope image of QD Ink-jet printing of lines and dots

After achieving size control, QD ink need to be dropped repeatedly inside the cell (surrounding by gray/black matrix) to increase the thickness for better blue light absorption and color conversion. In Fig 2, Various layers of red QD were printed and excited by the blue LED, and their emission spectrum were measured by a spectroradiometer (TOPCON Co.). The spectrum of QD printed 30, 36 and 60 layers are shown in Fig. 2. Two emission peak of 450 nm and 625 nm present the blue light LED emission and red QD emission. With the increasing layer thickness, the blue emission intensity reduced gradually. However, the red peak intensity is saturated after 36 layers. It is quite possible that the re-emission and re-absorption phenomenon between the QDs become dominant when we put too many layers into the same location. Therefore, the absorption is increasing but the actual QD peak intensity cannot be increased.

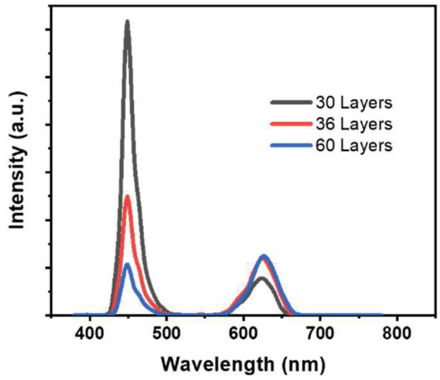


Fig. 2 Emission spectrum of a 20 μm QD pattern printed with increasing layers on a blue LED

When QD ink is dispensed into the cell, the surface tension between the gray/black matrix wall and the ink is different from the one between the substrate and the ink. Such difference can lead to non-uniform drying process. Thus uniformity issue is another challenge of QD ink-jet printing process which have been described in many studies [5, 8], such as coffee-ring phenomenon. To overcome this problem, we adjusted QD ink formula to lower its surface tension before depositing multi-layer.

2.2 QD photolithography

In the photolithography method, the QD layer is processed by material dispense, UV patterning exposure, and the development of the exposed material. In order to proceed a photolithography process of QD material, QD need to be well-dispersed in a photo-sensitive material (like photoresist). Here we formulated QD in the negative photoresist with 30 wt% QD as the same concentration as QD ink. QD photoresist (QDPR) was then spin-coated on the same glass/black matrix substrate, and exposed with a broad band aligner with 80 mJ dosage, and followed by developing with a 0.05 wt% KOH aqueous solution and post baking with 120 °C for 30 minutes. The QD patterns with 20 μm size were formed and excited with the same blue LED for their emission spectrum measurement. The result of emission spectrum of 20 μm QD pattern is shown in Fig 3, by photolithography process (Fig 3a) and ink-jet printing process (Fig 3b). Both QD patterns thickness are nearly 6 μm with the same height of black matrix.

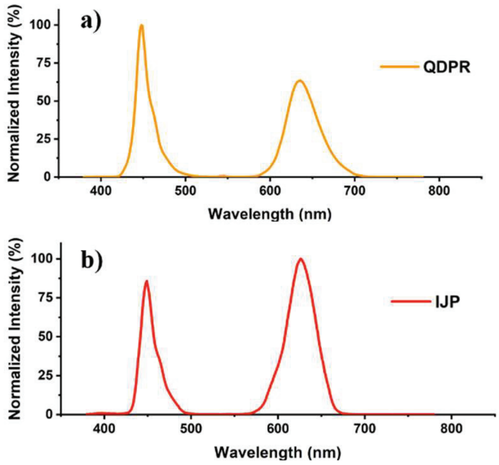


Fig. 3 Emission spectrum of QD pattern by (a) photolithography process (QDPR) and (b) ink-jet printing (IJP) process

	QD (in Toluene)	Ink-jet printing	Photo-lithography
Peak position (nm)	625	626	635
FWHM (nm)	36	38	43
LCE (%)	NA	67.7	57.0

Table. 2 optical properties of QD ink-jet printed pattern and photolithography pattern

3 Results and Discussion

The measurement results of QD pattern through photolithography (QDPR) process and ink-jet printing (IJP) process are shown in Fig 3, and their QD emission peak position, FWHM and light conversion efficiency (LCE) are shown in table 2. The LCE, which is different from the quantum efficiency or PLQY, is defined by the portion of converted light of total light out [9].

$$\mathrm{LCE} = \frac{\#\ of\ QD\ emitted\ photons}{\#\ of\ total\ detected\ photons} = \frac{\int_{QD\_band} \frac{\lambda}{hc} \times I_{em}^{QD}(\lambda) d\lambda}{\int_{total} \frac{\lambda}{hc} \times I_{em}(\lambda) d\lambda} \quad (1)$$

The original red QD in toluene, which is the normal storage solution for QDs, shows an emission peak at 625 nm and FWHM of 36 nm. After ink-jet printing of 60 layers, the peak shifted slightly to 626 nm and FWHM increased to 38 nm. This might cause by self-quenching of quantum dots. QDs absorb their red emission light especially at the shorter wavelength part in the emission band. When the printing layer increase, self-quenching becomes more severe. Thus red emission light intensity eventually saturates after 36 times of spray, which can be seen in Fig 2. This phenomenon also has been discussed in several studies [6, 10].

With the same QD material, QDPR pattern shows a red shifted and broadened peak compare to QD ink-jet printed pattern. The peak position red-shifted from 625 nm to 635 nm and the FWHM broadened form 36 nm to 43 nm. Since the thickness of QDPR and IJP pattern is similar, this result indicated that there might be some changes, either chemical or structural, of the QDs in the QDPR layer. Different from the ink, the solvent of negative photoresist we used has higher polarity. However, QDs are surrounded with nonpolar ligands, and thus they might become unstable in photoresist solution. Also, the exposure energy and alkaline developer during the photolithography process might damage the QD ligands and cause further aggregations.

From Table 2, we can also see that IJP pattern has a higher LCE of 67.7% compare with QDPR 57.0%. There are two possibilities lead to this result. First, the QD density of IJP pattern is higher. Solvent inside QD ink was evaporated after printing, and made ink-jet-sprayed QD stacked more in the same thickness compare to QDPR. Second, the damage to QD in photolithography during exposure and develop process might lead to the decay of conversion efficiency.

4 Conclusions

In this article, we compare the photonic properties of two types of quantum dot patterning process: Ink-jet printing and photolithography which are commonly applied in micro-LED color conversion process these days. QD are patterned in a glass/black matrix substrate with pitch/size of 40/20 µm via both IJP and QDPR method. The pattern thickness can be increased by stacking multilayers of ink for enhancing the blue light absorption and optimizing the QD conversion emission. We also compared the spectra of IJP and QDPR pattern with the same size and thickness. IJP pattern shows slightly red-shifted and smaller FWHM due to the better QD dispersibility and stability in the ink compare to the photoresist.

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