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Full Color Quantum Dot Light-Emitting Diodes Patterned by Photolithography Technology

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Abstract

Photolithography is a high resolution and mature patterning technique which has been widely used in semiconductor industry. For display application, a pixel consists of red (R), green (G) and blue (B) side-by-side sub-pixels, which thereby requires a high resolution patterning of the light-emission layers. In this work, photolithography is used to fine pattern the quantum dot (QD) light-emitting layers. To prevent the QDs being washed off during the lift-off process, the ZnMgO layer is treated by the hydrophobic material hexamethyldisilazane (HMDS). With HMDS treatment, the adhesion between the QDs and the ZnMgO is effectively improved. As a result, side-by-side RGB QD with pixel size 30 μm × 120 μm is successfully achieved. After patterning, the R, G and B QLEDs exhibit a maximum current efficiency of 11.6 cd/A, 29.7 cd/A and 1.5 cd/A, respectively.

Author Keywords

Quantum dots; light-emitting diodes; color patterning; high resolution; photolithography; HMDS

1. Introduction

Quantum dots (QDs) have a series of advantages, such as self-emitting, high color purity, color tunable, high quantum efficiency, good stability and simple solution-processability. Therefore, QDs are considered as one of the promising candidates for next generation display materials. After several years of development, light-emitting diodes (LEDs) based on QDs have made significant progress in terms of device efficiency and fabrication process [1-7], and its ultimate application goal is high-resolution dynamic full-color display. In order to achieve full-color QLEDs display, the light-emitting layers (EML) should consist of red, green and blue side-by-side EMLs, so the EMLs should be patterned with high resolution. Therefore, developing color patterning techniques for full color QLED display is highly demanded.

Ink-jet printing [8] and contact printing [9-12] have been used to fine pattern the QD layers. However, for ink-jet printing, because the evaporation rate of the edge solvent is faster than the center of the droplet, the printed films exhibit serious coffee ring effect. To eliminate the coffee ring, the viscosity, the surface tension and the boiling point of the solvents should be carefully tuned. Thus, the ink formulation is the key to the successes of ink-jet printing. For contact printing, the pattern will be limited by the size of the stamps, and transfer pressure uniformity is also difficult to control, which will increase manufacturing costs.

Recently, lithography was introduced to pattern the QLEDs. Researchers presented an alternative QD patterning technique using conventional photolithography combined with charge-assisted layer-by-layer (LbL) assembly to solve the trade-offs of the traditional patterning processes. The QLED device achieved maximum electroluminescence intensity of 23 770 cd/m2. [13]

In this work, we use photolithography to fine pattern the QD layers. Because it is difficult to etch the QD layer, lift-off is used during the patterning process. Reversal photoresist AZ5214E is used in the lift-off process. The AZ5214E photoresist can be used as positive photoresist after the first exposure, and can be used as negative photoresist after reverse baking and flood exposure. During the first exposure, the unmasked area can produce carboxylic acid which can promote the cross-linking reaction of the resin material during reverse baking. The cross-linked portion of the photoresist does not dissolve in the alkaline developer, in order to achieve the image inversion. The vertical section of the pattern formed by reversal photoresist is inverted trapezoid, which is favorable for acetone and photoresist reaction and removal during the lift-off process. To prevent the QDs being washed off during the lift-off process, the ZnMgO layer is treated by the hydrophobic material Hexamethyldisilazane (HMDS). HDMS is an interfacial modification material, after spin-coating HMDS in a heated substrate, HMDS produces a siloxane-based compound that can change the surface of the substrate from hydrophilic to hydrophobic. With HMDS treatment, the adhesion between the QDs and the ZnMgO layer is effectively improved. As a result, QLEDs manufactured by above series of methods can achieve a minimum pixel size of 30 μm × 120 μm, a maximum current efficiency (CE) of 11.6 cd/A (red), 29.7 cd/A (green) and 1.5 cd/A (blue).

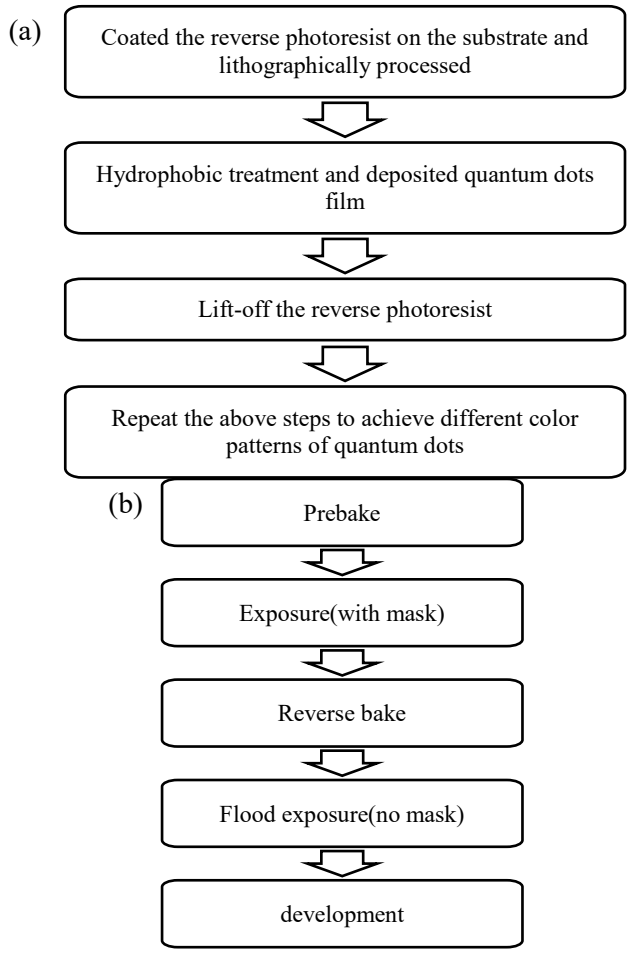
2. Experimental Detail

Inverted QLEDs with structure of glass/ITO/ZnMgO/QDs/TcTa (30 nm)/NPB (20 nm)/HATCN (10 nm)/Al were fabricated, where indium-tin-oxide (ITO), ZnMgO, QDs, 4,4′,4″-Tri(9-carbazoyl)triphenylamine (TcTa), -BIS(3-METHYLPHENYL)-N,N-39 (NPB), dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN), and Al work as cathode, electron transport layer, light emitting layer, electron blocking layer, hole transport layer, hole injection layer, and anode, respectively. ZnMgO NPs were deposited onto the ITO-coated substrate from a 20 mg/ml solution by spin-casting, followed by baking at 130 °C for 10 min. To pattern the QD layer, lift-off technique is used. First, reversal photoresist AZ5214E was spin-coated onto the ZnMgO layer, prebaked at 90 °C for 90 s, exposed with mask for 3.5 s, reverse baked at 120 °C for 2 min, flood exposed for 20 s, developed in rzx-3038 developer for 2 min and finally soaked in deionized water for 10 s. The process of reverse photolithography is shown in Figure 1 (a). And then, to increase the adhesion of QD, the samples were treated by HMDS vapor. After treatment,

commercially available CdZnSe/ZnS red QD with emission wavelength at 630 nm were spin-casted at 3000 rpm, followed by drying at 100 °C for 5 min. The samples were immersed in acetone and sonicated for 10 s to lift-off the photoresist and the QDs attached to the photoresist, and then immersed in methanol to remove excess acetone. The above processes were repeated in order to pattern CdZnSeS/ZnS (green) quantum dots light emitting layer and CdZnSeS/ZnS (blue) quantum dots light emitting layer. The lift-off processes are shown in Figure 1 (b). After patterning the R/G/B QD layers, the samples were transferred to a vacuum evaporator for thermally evaporating the organic charge transport layer and cathode at a base pressure of 5×10-4 Pa. The structure of devices is schematically shown in Figure 2 (a).

3. Results and discussion

Figure 1 (c)-(e) shows the images of the patterned QD layers. Figure 1 (c) shows the photoluminescence (PL) image of 30 μm×120 μm rectangle pixels on glass substrate. Figure 1 (d) shows the PL image of 320 μm×320 μm square RGB pixels on glass substrate, which consists of 80 μm × 320 μm rectangular sub-pixel with 40 μm spacing between each color. By further depositing other functional layers, electroluminescent (EL) devices with QD layers patterned by the same process can also be obtained, as shown in Figure 1 (e).



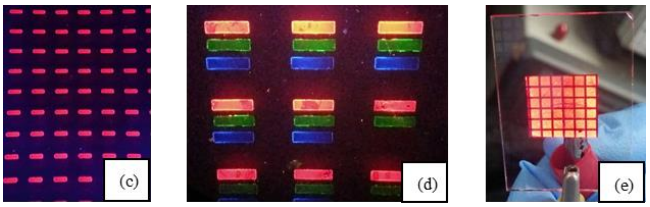


Figure 1. (a) Process of reverse photolithography. (b) Process of fabricating light emitting layer patterning device. (c)-(d) PL images of patterned QDs on the substrate with 405 nm laser as excitation source. (e) EL image of patterned QDs device at a bias voltage of 6 V.

Figure 2 shows the structure of the QLED and the energy level alignment of the devices. As shown in Figure 2a, the inverted QLEDs were fabricated with the structure of Glass/ITO/ZnMgO/ QDs/ TcTa/ NPB/ HATCN/ Al. The energy levels of each material are well matched, which could effectively facilitate the injection of electrons and holes from the electrodes. To evaluate if the patterning processes degrade the light-emitting efficiency of the QDs, device characteristics of QLEDs with and without patterning were measured. As shown in Figure 3 (a), after QDs patterning, the PL intensity is reduced by ~51%, which indicates that the QDs are damaged during the patterning process. Figure 3 (b) shows the CE-current density characteristics of the devices. Similar with the change of PL intensity, the efficiency of QLEDs is decreased from 15.8 cd/A to 10.3 cd/A after the patterning process. The decrease of PL and EL intensity are likely due to the removal of QDs during the lift-off process. This is because the QDs are subjected by multiple solvents treatments such as spin-coating photoresist, washing in acetone and ultrasonic during the lift-off process. The ultrasonic rinsing process can also accelerate the removal of QDs.

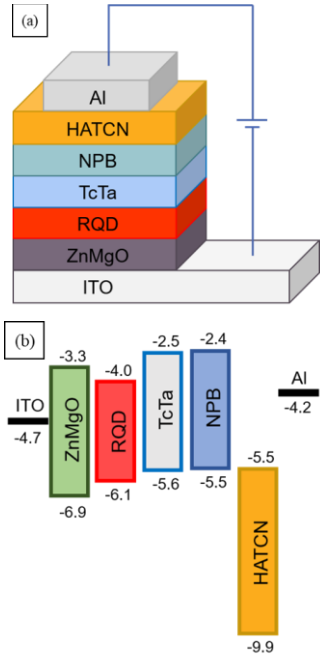


Figure 2. (a) The structure of the QLED. (b) Energy level alignment of the devices.

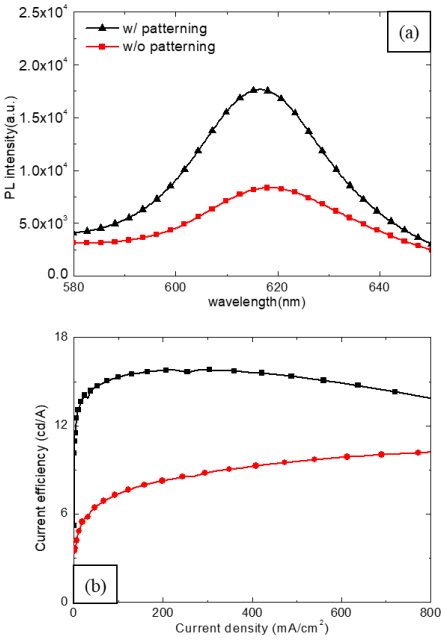


Figure 3. Device characteristics of the QLEDs with and without patterning (a) PL intensity. (b) CE-J. Due to the damage of lift-off process, the devices exhibit lower luminance and CE.

To address this issue, HMDS is used to treat the surface of ZnMgO. HMDS is a common adhesion promoter, which is widely used to improve resist wetting and adhesion. Figure 4 shows the water contact angle of ZnMgO film which was treated by HMDS. HMDS reacts with OH- on the substrate surface at high temperature and generates silyl ethers. The methyl groups of the HMDS fragment thereby form a hydrophobic surface and thus improve resist wetting and adhesion. It can be clearly observed that the contact angle of ZnMgO films is increased gradually with increasing HMDS treat amount and time, and the maximal contact angle is 67.8° when the ZnMgO is treated by 100 µL HMDS and annealed in atmosphere for 5 minutes. With HMDS treatment, the ZnMgO exhibit strong hydrophobic property and thereby QDs can better adhere to the surface of ZnMgO film.

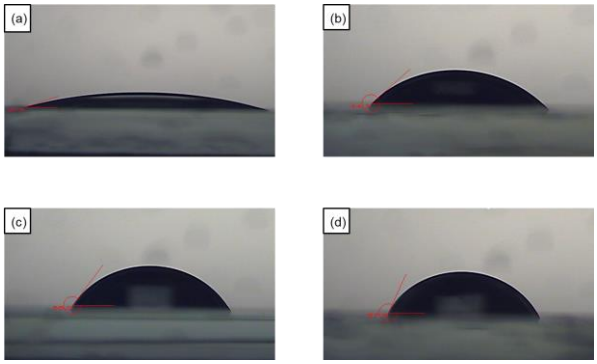
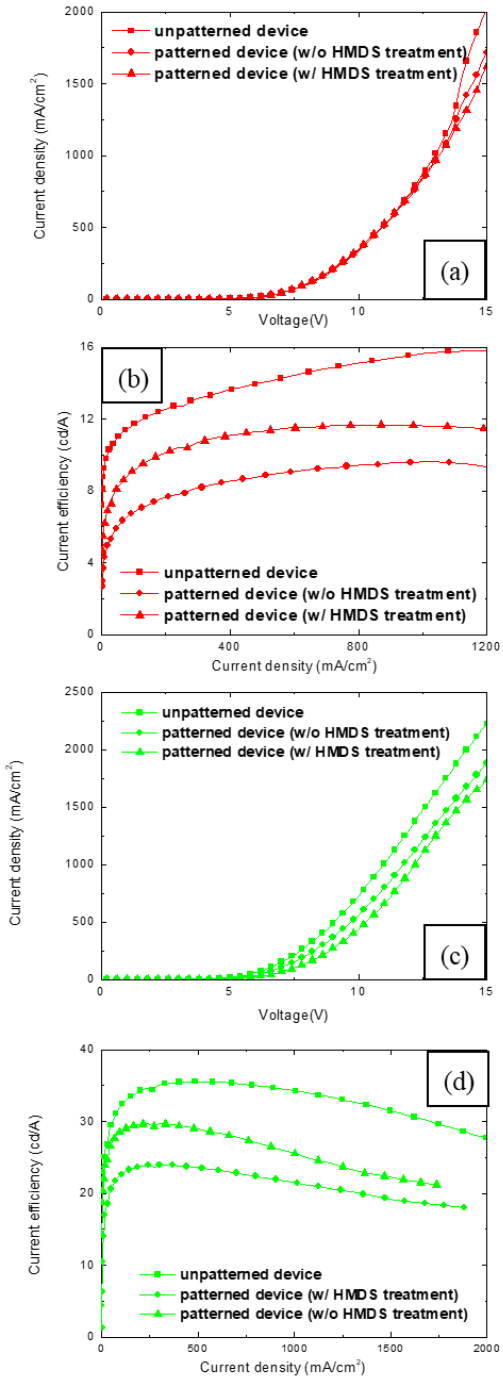


Figure 4. Water contact angle of ZnMgO layer with different HMDS processing conditions. (a) w/o HMDS. (b) 40 µL HMDS treat for 2 min. (c) 80 µL HMDS treat for 3 min. (d) 100 µL HMDS treat for 5 min.

Figure 5 compares the characteristics of QLEDs with QD layers treated by different conditions. The patterned devices still exhibit lower performance than the unpatterned devices. However, after HDMS treatment, the performances are improved. For example, the CE is effectively improved from 9.6 cd/A to 11.6 cd/A (red), from 23.9 cd/A to 29.7 cd/A (green) and from 0.9 cd/A to 1.5 cd/A (blue), revealing an enhancement factor of 18%, 20% and 40%, respectively. The improvement is preliminarily attributed to the better adhesion of QDs and thus less damage during the lift-off process. Studies of the detailed mechanisms are still on going.



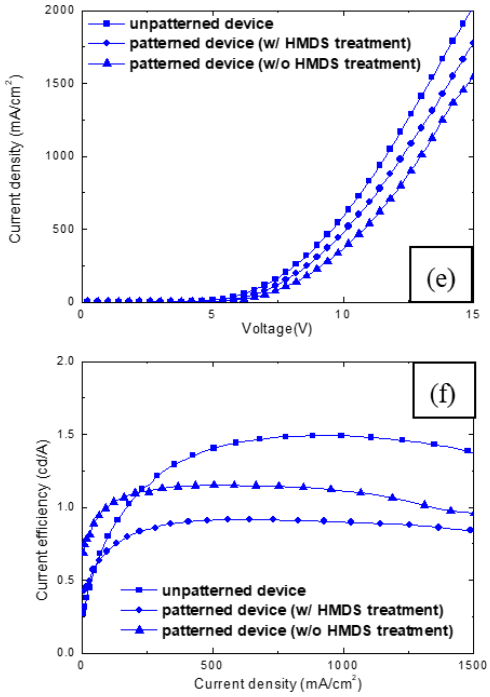


Figure 5. Characteristics of R, G, B devices with QD layers treated by different conditions. (a)-(b) Red devices. (c)-(d) Green devices. (e)-(f) Blue devices. (a), (c) and (e) J-V. (b), (d) and (f) CE-J

4. Conclusion

In summary, the QDs can be fine patterned by photolithography technology. Reversal photoresist AZ5214E is used which can generate inverted trapezoidal structure after exposure and developing and thus facilitate the subsequent resist lift-off process. With HMDS treatment, the QDs can better adhere to the ZnMgO surface, and thus can effectively resist the acetone and ultrasonic damage during the photolithographic process. As a result, patterned QLEDs achieve a minimum pixel size of 30 μm × 120 μm, maximum CE of 11.6 cd/A (red), 29.7 cd/A (green) and 1.5 cd/A (blue).

5. Acknowledgements

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