Quantum Dot Light Emitting Device by Photolithography

*Fuxing Jiao, Fengjie Jin, Liang Su, Shuaishuai Liang, Zhimin Yan, Wangfeng Xi, Xiujian Zhu**

***Visionox Technology Inc.**

Abstract

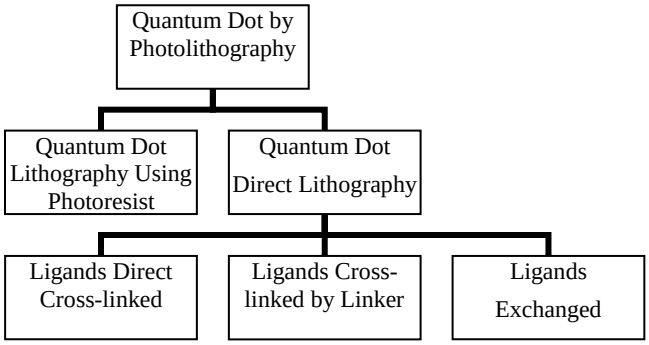
Recent years, an increasing number of research papers on quantum dot lithography have been published in more and more academic and industrial journals. This technology has attracted significant attention and study due to its technical advantages, such as high pixel density, brightness, and long lifespan. Notably, the acid-free direct photolithography quantum dot technique exhibits superior device efficiency and lifespan while offering a wide range of options for crosslinking agents and cross-linked ligands. Additionally, we have successfully developed a 1.42 inch 200 PPI QLED panel base on full color (Red, Green, Blue), manifesting the potential application of this technology in display.

Author Keywords

Direct Photolithography; Patterned; QLED;

1. Introduction

With the continuous development of technology, people's demand for color is gradually increasing. Quantum dots, which benefits from its quantum confinement, have small Full Width at Half Maximum (FWHM), thus wide color gamut. Besides, high life span and brightness are another advantages of QLED, making it as a highly promising next-generation display technology. Due to the organic ligands outside their unique core-shell structure, quantum dots are often deposited using solution processing. As for pattern technology, there are inkjet printing, electrophoretic deposition, transfer printing, lithography and so on. Among them, inkjet printing technology is most widely used. However, due to the constriction of the nozzle size and droplet precision, the pixel pitch index (PPI) of inkjet printing is limited. So it is more suitable for monitor and TVs. While lithography is known as a high resolution pattern solution in semiconductor area. The lithography of quantum dot also has small pixel width and pixel space. Even a PPI reach to 3994 has been reported. This may result in high opening area, which means high brightness and long lifetime. Quantum dot lithography technology can be divided into two categories: quantum dot lithography using photoresist and direct quantum dot lithography, here we will review about these process.



Scheme 1. Classification of Quantum dot Photolithography

2. Quantum dot lithography using photoresist

Xiao Wei Sun[1] et al. incorporated the commonly used photoresist AZ5214E into quantum dot patterning technology, utilizing it as a negative photoresist to develop quantum dots in the non-exposed region and subsequently removing the photoresist in the exposed region. Despite RGB-arranged quantum dot patterns are achieved through this method, challenges such as poor morphology of pattern edges and low optical efficiency still exist. In order to mitigate the impact of the photoresist developer on quantum dots, Xiaoguang Xu[2] et al. employed polyvinylpyrrolidone (PVP) as a sacrificial layer before quantum dot layer, then coating it with a patterned photoresist through photolithography. Subsequently, O2 plasma etching is introduced and the PVP not under the photoresist is etched. After depositing the quantum dot layer and stripping off the leaving sacrificial layer using a developer solution orthogonal to the quantum dots, a patterned quantum dot layer is left on the glass. However, this approach needs more stringent selection of sacrificial layer materials that are both orthogonal to QD and do not interact with either the photoresist or its developer, significantly limiting its applicability.

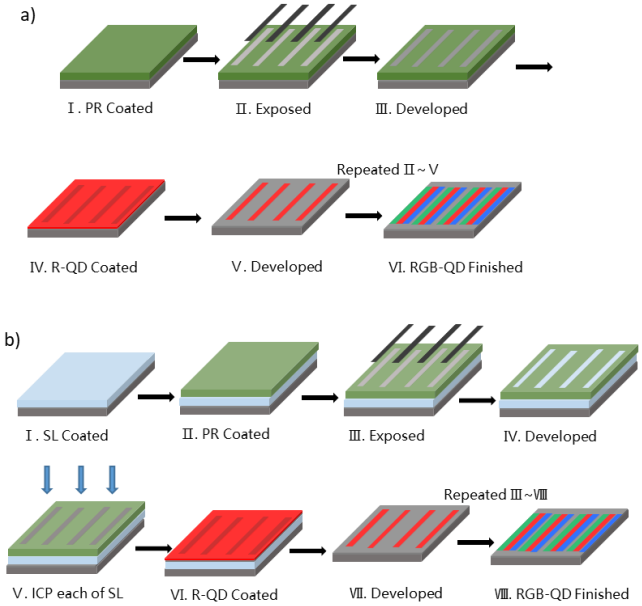


Figure 1. Quantum dot lithography using photoresist technological process. a) Without SL. b) With SL.

3. Quantum dot direct lithography

3.1. Process of direct lithography

Direct lithography of quantum dots means the ligands of neighboring QD are crosslinkered, thus the film can be left because of the reduced solubility. So we can call the QD film as a negative glue. The process of this technology is as shown in figure 2, there is no photoresist employed. And by repeating the pattern process of red, green and blue pixel, the full color pattern can be realized for display. Theoretically, the edge morphology of QD film is well due to the small film thickness of QD (usually < 50

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nm) and the performance of QLED can be reserved as much as possible.

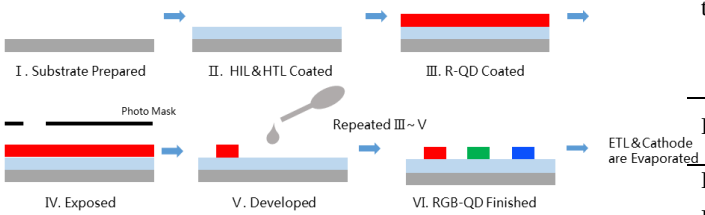

Figure 2. Quantum dot direct lithography technological process.

3.2. The type of direct lithography quantum dots

For detailed description, there are three type of direct lithography till now.

At early age from 2006-2011, some researchers reported the quantum dot direct lithography technique, which utilizes high-energy ultraviolet light or electron beam to induce C=C bond or C-H bond cleavage in oleic acid ligands on the surface of quantum dots for patterning purposes[3-5]. However, this method resulted in significant damage to the quantum dots due to the high doses with high energy and prolonged exposure time. Unfortunately, the performance of Device base on this patterned type is not satisfactory. So less papers can be found in the next six years.

Until 2017, Dmitri V. Talapin et al. [6-7] elucidated the mechanism of ligand exchange in quantum dots for the first time, providing a comprehensive database on ligand exchange and offering detailed insights into the reaction mechanism and process parameters. This groundbreaking work is considered a pivotal milestone in the field of quantum dot direct lithography. Under specific conditions involving light and acid, a ligand exchange takes place between photoacid generator (PAG) and QD ligands, changing the solubility of QDs and leading to patterned film. The distinctive feature of this technical approach lies in its predominant utilization of PAG groups as ligands, resulting in H^+ release upon exposure to light. As we know, H+ ion is an electron acceptor that can quench the exciton. Therefore it may result in an increase in non-radiative QD transition rate accompanied by a decrease in luminous efficiency.

To reduce the effect of acidic conditions on quantum dots, Moon Sung Kang et al. introduced aryl azide fluoride as a crosslinker into QD to enhance its functionality.[8-9] When exposed to low energy light, aryl azide fluoride undergoes nitrogen carbene formation and subsequently reacts with the surface ligands of QD through oxygen insertion reaction, resulting in a patterned film. This approach exhibits broad applicability to quantum dots, suggesting that theoretically any QD surface ligands containing C-H bonds have the potential for pattern formation. However, due to its poor conductivity, the crosslinker is limited at low doping concentration to gain a high device efficiency and low voltage. Besides, whether the linker is dispersed uniformly in QD film is not known yet. Consequently, a fully cross-linked film is hardly to attained, and the small amount of QD will be moved during developing stage. To address this issue, Wan Ki Bae et al. [10] conducted ligand exchange between a photosensitive ligand containing benzophenone and the dispersed ligand on the surface of quantum dots. Once again, only low exposure energy was needed as the ketone group reacted with C-H bonds on the ligand to form patterns. The mode, we call “ligand exchange cross-linking” guarantee the uniform dispersion of linkers and causes little damage to QD film layers during developing. Fortunately, it does not introduce surface defects in quantum dots which can reduce overall efficiency. Therefore, the devices base on these two types can achieve high levels.

Table 1. Comparison of three direct lithography methods of quantum dots.

Direct lithography method	Characteristic	Device efficient
Ligands Direct Cross-linked	Ligands destroyed	Low
Ligands Cross-linked by Linker	unknown disperse	High
Ligands Exchanged	uniformly disperse	High

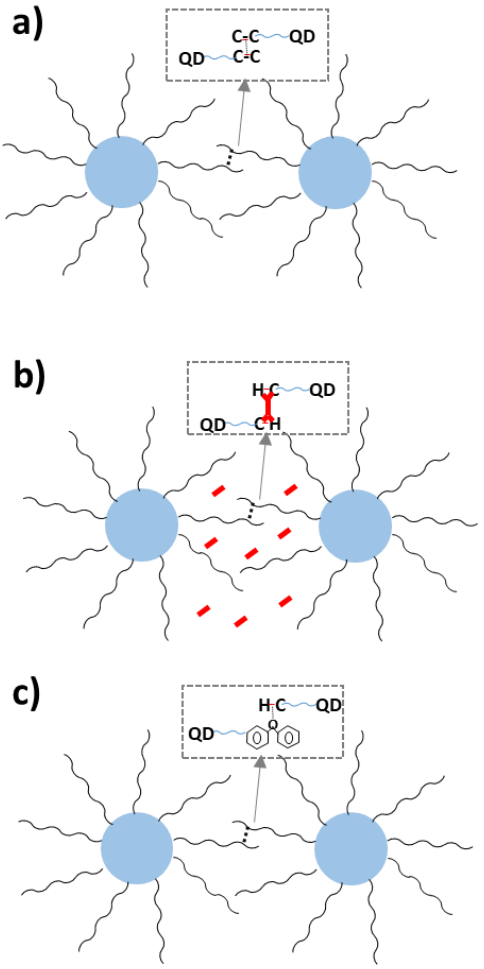

Figure 3. Diagram of three reaction types. a) Ligands Direct Cross-linked; b) Ligands Cross-linked by Linker; c) Ligands Exchanged.

3.3. The type of linker of quantum dots

Here, we compare and analyze the reaction principle as well as the advantages and disadvantages of photocrosslinked groups. Under light irradiation, the azide group undergoes photolysis to generate nitrogen carbene, which then reacts with C-H bonds on the ligand surface of QD to complete cross-linking. The synthesis method for such photocrosslinked groups is straightforward; however, high doping content can lead to a loss in QD photo-luminescent quantum yield (PLQY). Ternary carbon heterocycles also generate carbon carbene upon photolysis, similar to nitrogen carbene.

Carbon carbene reacts with C-H bonds on the ligand surface of QD for efficient cross-linking. As a singlet carbene species, carbon carbene exhibits better stability in solution and faster crosslinking with QDs. However, due to its small $\triangle E_{st}$ to triplet, it is more sensitive to oxygen and requires strict control over oxygen content. Aromatic ketone derivatives are hydrogenated to form ketone groups that subsequently undergo hydrogen intercalation reactions with QD surface ligands for cross-linking purposes. Generally speaking, aromatic ketones exhibit slower reaction rates often involving photothermal synergistic reactions requiring longer exposure times; however, modification with certain electron-absorbing groups can accelerate their reaction rates. Due to its unique molecular structure, thiol groups can only undergo hydrogen intercalation reactions with C=C bonds for completing cross-linking processes; therefore they have higher requirements for specific types of surface functional groups on QDs.

Linker photosensitive groups	Characteristic
Azocarbene	Fast cross-linked rate; Ligands wide selection
Carbene	Fast cross-linked rate Sensitive to O_2
Aromatic ketone	Ligands wide selection; Medium reaction rate
Sulfhydryl	Ligands limited; Badly stability

Table 2. Comparison of photosensitive groups of quantum dots.

4. Research progress of quantum dot direct lithography

According to the knowledge above, we present a QLED display utilizing direct lithography quantum dots, which exhibits promising performance. As shown in figure 4, the 1.42-inch prototype full color (red, green, blue) display has been realized with a PPI of 200. This manifests the possibility of lithography quantum dots in display.

Figure 4. 1.42-inch QLED display.

5. Conclusion

In summary, quantum dot lithography technology is capable of meeting the requirements for large size and high PPI preparation. However, the technology scheme involving quantum-dot exchange or cross-linking under non-acidic conditions exhibits broad selectivity and minimal damage to quantum dots. Nevertheless, there are still certain challenges that need to be addressed, such as achieving uniform dispersion of crosslinking agents and enhancing the binding strength between optical crosslinked ligands and quantum dots. These challenges present new demands and obstacles for optical crosslinked materials and quantum dots, necessitating further exploration of materials and processes. Though we fabricate a 1.42-inch prototype QLED display, there are still many issue to be solved for industrial application

6. References

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