PROCEEDINGS OF THE INTERNATIONAL DISPLAY WORKSHOPS, VOL.29, 2022

Recent Progress of Cd-Free Quantum Dot Electroluminescent Display

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Keywords: Quantum dot, electroluminescence, inkjet-printing

ABSTRACT

Recently, QD (Quantum Dot) OLED Displays were released in the market with quite outstanding image quality. As a result, QD Technologies have attracted great attention in academia and industry, as OLED technologies did. In this paper, it will be discussed recent issues and progresses of the QD Electro-luminescent display (QD-LED) about QD materials, devices and inkjet technologies.

1 Introduction

Recent display trend has changed from ‘Bigger’ to ‘Better’. Rather than the display size and resolution, the color, HDR and contrast ratio is regarded much more important features of the display. This trend is reflected by continuously increasing market share of self-luminous displays such as OLED and QD OLED displays. Among these displays, the QD OLED attracted the market because it takes advantages of both of QD and OLED, such as deep colors, true black, high luminance as well as wide viewing angle in the same display panel (Figure 1).[1,2]

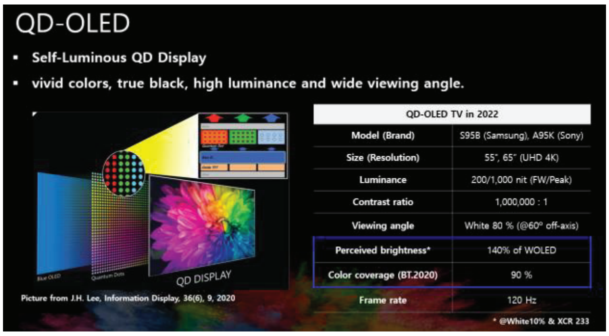

Figure 1 QD OLED Display

Inkjet-printing has been regarded as the most suitable tool for depositing liquid materials on substrates in a display manufacturing process. It can greatly reduce a material consumption, precisely control the thickness less than 50 ㎛ and freely form any patterns, without any fine-patterned mask. Because of these advantages, it has been utilized for ‘area-printing’ of liquid crystal, polyimide for LCD and monomer of thin film encapsulation for OLED display since 2008.[3] Recently, the inkjet printing expanded its application to ‘pixel-printing’ of QD color conversion layers in QD OLED since 2021. Now, pixel-printing is regarded as a proven tool for patterning RGB materials in self-luminous display, which enables a low cost manufacturing on Gen 8 mother glass.[3] As a next step, the pixel-printing is believed to be used for patterning RGB EMLs in self-luminous displays. Actually, many display panel makers have demonstrated RGB OLED and QD-LED panels, which employed the pixel-printing technology for patterning RGB EMLs.[4]

It is very difficult to inkjet-print EL(electroluminescent)-QD inks for the QD-LED than QD OLED, which originates from the differences of the drop size, thickness, need for multi-layer and electro-luminescent functions. New technical challenges arise from these distinctions of printing ink materials. Next section deals with these issues in more detail.

2 Key Issues in QD-LED Display Technology

The QD-LED display has a similar device structure as the inkjet-printed OLED display. As a result, same technical issues need to be solved, such as an ink formulation for stable jetting, uniform dried layer, intermixing control and so on. But, the colloidal nature of QD inks adds additional challenges that do not exist in the inkjet-printed OLED.

2.1 Cd-free QD Materials

EL-QD produces excitons inside it from electric charges injected from adjacent charge transport layers unlike PL(Photo-luminescent)-QD. This nature requires very thin EL-QD layer around 30 nm to minimize electric resistance. As well, relatively short ligand with thick shell is demanded for easy injection of electric charges to QDs and good charge balance, compared to PL-QD. On the other hand, PL-QD requires high loading of QD materials and light-scattering agents for high blue light absorption, which results in very thick layer up to 10 ㎛. This demands different approaches to design QD synthesis, ligand structure and ink formulations.

2.2 Current Status of Cd-free QD-LED Devices

It is well-known that Cd-based QD-LEDs surpass Cd-free QD-LEDs in terms of device efficiency and lifetime.[5] However, many researchers have been accelerating the R&D to improve the device performances of Cd-free QD-LEDs, because it is not possible to use Cd-based QDs in consumer electronic

ISSN-L 1883-2490/29/0909 © 2022 ITE and SID

applications in EU, according to a strong regulation based on RoHS directive. Figure 2 and 3 show a progress of a EQE and T50 lifetime of Cd-free QD-LEDs since 2012.[5] It is quite obvious that Cd-free QD-LEDs are quickly closing the performance gap. However, there is still a big gap in the device lifetimes of Cd-based and Cd-free blue QD-LEDs. It is because a new core like ZnTeSe is required for Cd-free blue QD, unlike red and green QDs which are based on conventional InP-based PL-QDs.[6-8] It is highly requested to find ways to improve the lifetime of the Cd-free Blue QD-LED. Additionally, it should be noted that all of these performances are of spun-coat devices and inkjet-printed OLED panels showed lower device performances than spun-coat ones, because of intermixing, non-uniform layer thickness inside pixel and so on.[3] The gap must be overcome between spun-coat devices and the inkjet-printed panel, too.

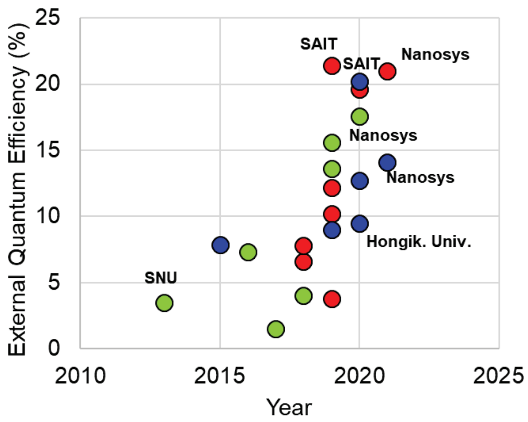

Figure 2 Progress of Cd-free QD-LED efficiency

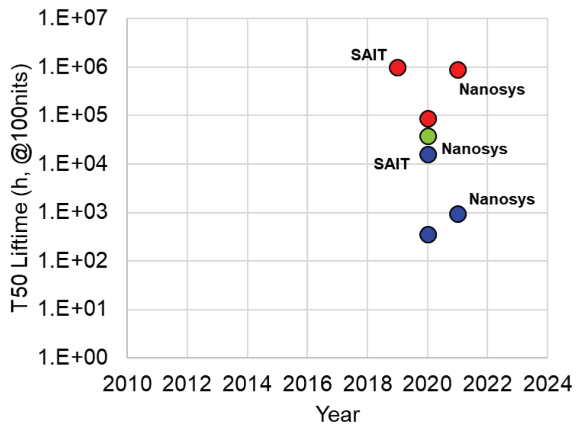

Figure 3 Progress of Cd-free QD-LED lifetime

2.3 Colloidal Inks for QD and ETL

Good ink needs to meet many requirements such as jetting stability, head/tube suitability, as well as jetting and drying properties. Such ink can be developed by careful design of an ink formulation. It requires a balanced combination of surface tensions, viscosities and vapor pressures of solvents, with proper choice of the inkjet head and jetting waveforms. Frequently used metric which decides the goodness of inks is Ohnesorge (Oh) number, which means the ratio of viscous force to surface tension. If the reciprocal of Oh number for an ink is between 1 and 10, the ink seems to be jettable and not to form satellite drops.

However, unlike inks without any particulates, colloidal inks easily clogs inkjet head nozzles, even though they meet Oh number metric. For example, A. Lee et al reported in the identical Oh^{-1}-range from 2.5 to 26, non-jetting and nozzle clogging were observed for some ZnO colloidal inks.[9] They showed this problem could be overcome by adding polymeric dispersant with the content properly optimized.

However, the organic dispersant deteriorates the electric function of the dried film of colloidal inks, because it remains inside the film so as to retards the electric current even after drying solvents. Thus, it is highly desired to minimize the content of organic dispersant in the dried film, while retaining the colloidal stability. We successfully achieved this task for a QD ink by introducing short alkyl chain ligand with highly strong anchoring group. As shown in Table 1, the strong anchoring group of the ligand increased the organic content, which means high surface coverage of the ligands, even though the alkyl chain length is reduced for lowering the electrical barrier between QDs. In practice, the QD ink B with the new ligand was remained stabilized until 30 days after ink loading, compared to 3 days of an original ink (Figure 4).[10]

Ligand	QD ink A	QD ink B
Anchor	-COOH	-SH
Alkyl-chain	Long	Short
Content	11.2%	14.2%

Table 1 Ligand properties of the QD inks

In addition to the jettability, another important guideline for colloidal QD inks is to minimize damage to colloidal materials. In reality, we found out a metal impurity and polarity of solvents severely degraded the PL quantum yield of QD in a solution and solid phase. To solve this issue, we purified QD solvents and used less polar solvents for ETL ink, which was deposited on QD film.[10]

Like inkjet-printed OLED layers, inkjet-printed QD films also suffer from non-uniform thicknesses inside pixel area. It is well-known that films with non-uniform thickness results in lower efficiency, short lifetime and deviation from targeted color than flat film. Non-uniformity of film thickness originates from unidirectional ink flows inside the pixel, caused by the different drying rate around drop surface. First solution is to make an inverse flow by using Marangoni flow, which means the fluid flow from low to high surface tension area. Marangoni flow can inverse the normal flow, only when the surface tension gradient is very large inside the ink. Thus, it is practically difficult to find proper solvent combinations to meet other ink requirements like ink-jettability, good spreading on under-lying layers, no intermixing and so on. Another option is to increase the viscosity of the ink when it arrives at the flat shape during drying process, in other words, a gelation of the ink. It is possible by adding high viscosity or low solubility solvents to the ink, but it might cause jetting failure or nozzle clogging as side effects.

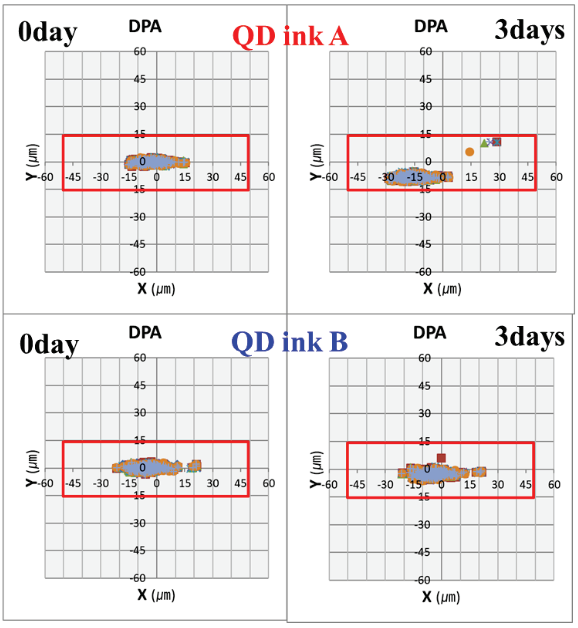

Figure 4 Drop placement accuracies of QD inks

Intermixing is a well-known phenomenon in solution-processed organic electronics. It happens when the ink solvent dissolves an upmost layer, which alters device performances of electronic devices such as OLEDs, OPVs and QD-LEDs. To overcome this problem, two approaches are proposed, of orthogonal solvents for inks and cross-linking of upmost layer. Both of the methods are proven to work for QD-LEDs, too.[12-13]

2.4 Inkjet-printed Cd-free QD-LED Display

Recently, we fabricated a 6.95” 217 ppi Oxide TFT-based QD-LED panel by inkjet-printing of Cd-free QD and charge transporting layers (Figure 5). InP QD inks for Red and Green colors, and ZnTeSe QD ink for Blue colors were developed for inkjet-printed EMLs in the QD-LED device. ZnMgO nanoparticle ink was also developed for inkjet-printed ETL, with organic inks for HIL and HTL. A top emission device structure was employed for 217 ppi pixel resolution, with fine tuning of an electrical charge balance and optical micro-cavity design.

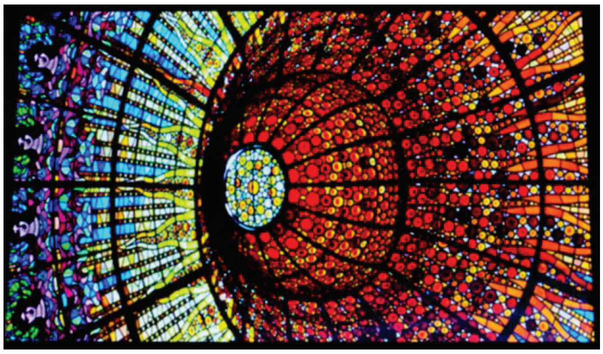

Figure 5 6.95” 217 ppi inkjet-printed Cd-free EL-QD

3 Conclusions

In this report, recent trends and key technical challenges are discussed of inkjet-printed Cd-free QD-LED developments. In addition, our recent progress is demonstrated to improve the inkjet process and device performances of Cd-free QD-LED display. Our efforts are ongoing to overcome the remaining technical issues.

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