High Performance Black Bank for Ink-Jet Process Seishi Shibayama¹, Daishi Yokoyama¹, Tadashi Kishimoto¹, Teruaki Suzuki¹, Atsuko Yamamoto¹, Julian Burschka²

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¹Merck Electronics Ltd, 3330 Chihama Kakegawa-City 4371412 Shizuoka Japan ²Merck KGaA, Darmstadt, Germany. Frankfurter Str. 250 DE-64293 Darmstadt Keywords: photolithography, black bank, low temperature, optical density, wettability.

ABSTRACT

Due to the evolution of new technologies, a change in properties and performance has recently been demanded for the black material typically used as a sub-pixel divider in displays. This talk will discuss the process from patterning to ink filling for a black bank material designed for ink-jet applications and review the critical functionality required for outstanding visual quality in future displays.

1 Introduction

The Black material, which has optical properties that avoid any significant light transmission, is used as a partitioning material to separate red, green and blue subpixels of a display. Next-generation displays such as the combination of quantum dot pixelized color converters with an OLED back light -referred to as QD-OLED- and QDbased micro-LED require bank materials with several special features due to their unique display structures [1-3]. Therefore, those display architectures also have different requirements for material performance compared to previous technologies. Far and foremost, a rather thick bank structure is required. For QD-OLED displays a thick film is more advantageous for a high light conversion efficiency. And elevated thickness is also required for Micro-LED Display because the bank needs to provide enough room in which the LED chips can be installed. In addition, for both applications, the optical density (OD) must be high to prevent RGB color mixing and the bank material needs to be patternable by photolithography. Ideally the pattern shape of the bank should be vertical under-cut shapes, footing and tapered shapes are undesirable. In the process of filling pixels with QD ink for the QD-OLED technology, the top bank surface must be able to sufficiently repel the QD ink, whereas good wetting of the QD ink on the bank's sidewall ensures complete filling.

Recently, from the viewpoint of the manufacturing process, there is also a need for a technology to cure the bank at low temperature so as not to damage underlying components. If the pixel color converter parts and the TFT part are provided on separate glass substrates, high temperature cure is acceptable. However, if the TFT parts and the converter parts are made on the same substrate, low temperature cure baking may become critical. In the present communication, we will demonstrate that most of those challenges can be addressed by material design and demonstrate the preparation of black banks that can be cured at low temperatures and provide suitable wetting properties for QD ink filling by ink-jet printing.

2 Experiments

2.1 Preparing patterning substrate

The bank of the pixel color converter should have low transmittance at typical RGB wavelengths to prevent RGB light from mixing at sub-pixel level. We formulated the patterning material with a black filler material to achieve sufficiently high OD at a film thickness of 10 µm (sample 1). Two substrate types are prepared for the evaluation: one is an un-patterned substrate for optical density and contact angle measurements. The second is a patterned substrate for pattern profile and QD-ink filling tests. The patterned substrate was prepared by the following procedure. The prepared black bank formulation was applied onto a 4-inch glass wafer while the substrate was rotated at a specific speed to obtain a thin film (spin-coating). It was then placed on a hotplate at 90°C and baked for 120 seconds. After that exposure was carried out, the substrate was dipped for 100 seconds in a low concentration alkaline developer and rinsed with distilled water for 30 seconds. Finally, the substrate was heated on a hotplate at 90°C for 30 minutes to accelerate curing.

2.2 Equipment

A spin-coater MS-A100 (MIKASA) was used for application. A hot plate HHP-411V (AS ONE) was used for baking. Film thickness was measured with Dektak XT (BRUKER). A stepper NES2W-ghi06 (Nikon) was used for exposure. For the photomask in the exposure process a pattern design with a line width of 15 µm and sub-pixel area of 150 µm x150 µm was used. The pattern was observed with an optical microscope **MX61A** SEM JSM-7100 (OLYMPUS) and (JEOL). Α spectrophotometric colorimeter CM-5 (Konica Minolta) was used for UV-Vis spectra measurement. Contact angle was measured with a DM-700 (Kyowa interface Science). For wetting tests, the volume of liquid was adjusted to 3 µl and dropped onto the substrate coated with the film. For the QD-ink dropping/filling tests, inhouse made green QD-ink was used. The surface tension was set to around 30 mN·m⁻¹ and the liquid volume was adjusted to 10 pl. An ink-jet tool Dimatix (Fujifilm) was used to fill QD-ink. The QD-ink was cured with 300 mW·cm⁻² of LED light for 10 seconds.

3 Results and discussion

3.1 Optical density & Contact angle

Table 1 shows results of the optical density. The optical density at a film thickness of 10 μ m was 2.0 at 460 nm, 2.2 at 540 nm, at 2.1 at 630 nm. The OD of our typical transparent film (sample 2) at film thickness of 15 μ m was 0.02 at 460 nm, 0.0035 at 540 nm, 0.0009 at 640 nm. Sample 1 exhibited much improved light shielding properties compared to such transparent materials.

The contact angles of distilled water (DIW) and CH₂I₂ 5 seconds after drop of liquid on film are shown in Table 2. The contact angles were DIW 99.8° and CH₂I₂ 82.4° at 20 mJ·cm⁻². The surface free energy (SFE) was 17.5 mJ·m⁻², which was calculated using Owens-Wendt theoretical formula. The contact angle and SFE were examined at different exposure dosage. At exposure doses of 20 mJ·cm⁻² and above, the contact angle remained stable at around 100°. The contact angle of DIW at 10 mJ·cm⁻² dropped due to insufficient curing of the film. The contact angle of CH₂I₂ was stable around 82° for all exposures. SFE also stabilized at about 17 mJ·m⁻² with an exposure of over 20 mJ·cm⁻². The range of variation of the contact angle after 60 seconds was investigated (Figure 1). Exposure of 10 mJ·cm⁻² is shown in purple, 20 mJ·cm⁻² in blue, 30 mJ·cm⁻² in green, 40 mJ·cm⁻² in yellow, 50 mJ·cm⁻ ² in pink and 80 mJ·cm⁻² in dark blue. The amounts of change at any exposure dose ranged from -2.0° to -3.0° for DIW and from -0.0° to -0.6° for CH₂I₂. This clearly shows that that the film maintained its high repellency after the drop.

	Table	1.	Optical	density	V
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		Wavelength (nm)				
		460	540	630		
Optical density	Sample 1	2.0	2.2	2.1		
	Sample 2	0.02	0.0035	0.0009		

Table 2. Contact angle and SFE

		Exposure dosage (mJ·cm ⁻²)						
		10	20	30	40	50	80	
Contact angle	DIW	92.0	99.8	99.1	101.9	100.3	101.9	
	CH2I2	82.4	82.4	83.0	82.4	83	82.4	
SFE (mJ·m⁻²)		19.8	17.5	17.5	17.1	17.2	17.1	



Figure 1. The correlation between contact angle and exposure dosage, (a) DIW, (b) CH_2I_2

3.2 Pattern profile

A cross-section SEM image of the pattern profile is shown in Figure 2a. The line width at top and bottom of the pattern at 20 mJ·cm⁻² exposure dose was 15.6 μ m and 15.0 μ m, respectively, confirming near-torectangular shape. To convert light from the backlight efficiently, the pattern shape should be vertical as an undercut shape or strong taper would lead to shadowing effects and loss in visual quality. The image also shows that there was no residue in the pixel area, which is detrimental to avoid pixel defects. Surface roughness might be another defective factor hampering good filling and visual quality. The surface condition of our films is shown in Figure 2b. We consider the surface smooth on both the top and sides of the pattern without any significant holes or localized features on the surface.





Figure 2. Pattern profile of black bank, (a) line and pixel hole, (b) top and side wall.

3.3 Chemical durability to PGMEA

Considering the post-processing, the black bank should be a solvent-resistant material in order to fill the QD-ink without any degradation and/or phase intermixing. For testing this property, the substrates were immersed in PGMEA for 3 minutes to investigate whether there was swelling and peeling. The condition of the patterning substrate before and after immersion in PGMEA for 3 minutes was observed by optical microscopy as shown in Figure 2. No lifting or peeling after immersion was observed. Also, no difference in line width and no distortion were observed due to swelling. The film thickness (FT) was 11.6 μ m before immersion and 11.5 μ m after immersion confirming that the film thickness was also unchanged.



Figure 3. Optical microscope image of grid pattern (150 µm x 150 µm space, 15um line), (a) before immersion, (b) after immersion in PGMEA for 3 min.

3.4 Wettability of QD-ink

From the viewpoint of proper filling by ink-jet printing, the ink should be repelled from the top surface of the pattern but demonstrate good wetting towards all faces inside the pixel volume. A film with insufficient liquid repellency would allow QD-ink to penetrate into the film. Additionally, overflow may occur easily if the ink has high affinity to the bank's top surface.

To observe the liquid repellency on the film and in the pixel, QD-ink was actually dropped on the film and in the pixel, and the droplet size was measured. The results of one drop of QD-ink on the film and in the pixel, respectively, are shown in the figure 4. The droplets were 46 µm in diameter on the bank and 80 µm in the pixel. In the case of a bank compositions with poor liquid repellency, QD-ink penetrated into the film (not shown here). To investigate the wettability of the pixel area in more detail, we evaluated how many drops of QD ink could wet the entire bottom of the pixel when QD ink was continuously dropped (Figure 5). The droplets maintained a spherical shape up to two drops whereas after the third drop, the accumulation of liquid in the pixel center collapsed and the entire bottom was wetted. Continuing to add droplets, the pixel became fully filled with QD-ink at 35 drops. It was confirmed that the QDink did not overflow even after 40 drops in the pixel.

The cross-sectional image after QD-ink filling with 35 or 40 drops and subsequent curing are shown in Figure 6a. The pixel was fully filled with 35 drops resulting in a nearly flat film surface. The QD film made with 40 drops clearly shows a convex top due to slight overfilling though without any visible ink overflow. In the empty pixels adjacent to the filled pixels, no QD material was found suggesting the QD-ink did not penetrate the bank. Observation of the boundary between the QD-ink and the Bank also revealed no bubbles (Figure 6b). A picture of the pixelated luminescent QD film under blue light excitation is shown in Figure 7 confirming strong contrast and sharp pixel edges.



Figure 4. One drop of QD-ink on the bank and in the pixel



Figure 5. Wetting of QD-ink when QD-ink was continuously dropped.





Figure 6. Cross-sectional image, (a) QD-ink filling with 35 drops and 40 drops, (b) boundary between the QD-ink and the bank.



Figure 7. Optical microscope image of QD-ink lighting.

4 Conclusion

We demonstrate the application of a black bank material designed for pixel color conversion applications and discuss critical requirements. The material is photopatterned even at elevated thicknesses, providing vertical pattern shape, high OD, and low temperature curing. Furthermore, we explain critical parameters for effective ink filling and show successful filling with a typical QD-ink. We believe that our developments demonstrate how material design can help to ease processing and aid to enable new breakthrough display technologies.

5 Reference

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