Development of Novel Photo-sensitive Light-shielding Bank with High Reflectivity for Next-generation Display

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A new display with quantum dot color filter (QD-CF) is attracting attention as a next-generation display. The QD-CF display can achieve high brightness, definition and contrast. It is essential for QD-CF structure to form “banks” separating QD materials.

In this paper, we introduce the novel photo-sensitive light-shielding banks with high reflectivity, which are suitable for QD-CF display. This bank material contains both TiO$_2$ pigment and UV transparent black pigment. The material can form gray banks which have a thickness of 10 μm with a good taper angle of 86°. The banks show good light-shielding property (transparency@450 nm<1%), high reflectivity of 50.8% at 550 nm, and high heat resistance (1% weight loss temperature is 353 °C). This developed material is ideal for application of QD-CF display.

Keywords: Photo-sensitive, Light-shielding, Reflectivity, Bank, QD-CF

1. Introduction

Currently, liquid crystal display (LCD) panel is the main technology for displays used in TVs, monitors, tablets, smartphones and other devices [1, 2]. However, one of the issues of LCD is that the light utilization efficiency becomes low because of absorbing the white back light by the color filter (CF) (Fig. 1 (a)).

Recently, quantum dot color filter (QD-CF) display technology [3-5] has attracted attention as one of the methods for improving the efficiency. QD-CF display uses the blue back light and QD-CF (Fig. 1 (b)). QD-CF is a CF of which color pixels are replaced from organic pigments to light scattering and quantum dot (QD) materials. These materials are filled in each pixel separated by “banks”. The blue pixel is filled with the light scattering material to pass through the blue light at a minimal loss. The green and red pixels are filled with QD materials to convert the blue light to respective light without large light absorption. Therefore, the light utilization efficiency of this display can be much higher than the conventional LCD in principle. In addition, it is expected that a
next-generation display for higher contrast and color gamut can be developed by combining QD-CF with blue back light of mini LED or micro LED, which is much smaller than the conventional LED.

It is important for QD-CF structure to form the banks separating the materials. The banks are required a thickness of about 10 μm with a good taper angle of 80°~90° in terms of the conversion efficiency of QD. In addition, the banks need to have not only good light-shielding property (transparency @450 nm <1%) but also high reflective property (reflectivity@550 nm>30%) in order to achieve high luminance of the display. Furthermore, the banks are required high heat resistance because it takes a high temperature (>250 °C) in a post-process such as a wiring connection process.

By the way, we have developed a photo-sensitive siloxane materials with high heat resistance and transparency for a long time [6, 7]. In addition, we have developed and mass-produced photo-sensitive white materials with high reflectivity using siloxane polymer and TiO₂ pigment as white decoration of touch panels.

In this paper, we introduce the novel photo-sensitive light-shielding banks with high reflectivity. This bank material is on the basis of the conventional white material, and contains both TiO₂ pigment and UV transparent black pigment. The material can form gray banks which have a thickness of 10 μm with a good taper angle of 86°. The banks show good light-shielding property (transparency @450 nm<1%), high reflectivity of 50.8% at 550 nm, and high heat resistance (1% weight loss temperature is 353 °C). This developed material is ideal for application of QD-CF display.

2. Experimental
2.1. Materials
We prepared the 6 types of photo-sensitive materials shown in Table 1.

Polymers, siloxane polymer and acrylic polymer, were synthesized at our company.

Pigments, TiO₂ pigment, carbon black pigment, and UV-transparent black pigment, were commercially purchased.

An acryl monomer, dipentaethritol hexa-acrylate (DPHA), was purchased from Nippon Kayaku Co., Ltd.

A photoinitiator, bis(2,4,6-trimethyl-benzoyl)phenylphosphine oxide (Omnirad 819), was purchased from BASF.

Additives which contain surfactant and adhesion promoter improve liquid repellency and adhesion to substrate.

As solvents, propylene glycol monomethyl ether acetate (PGMEA) was purchased from Kuraray Co., Ltd. Diacetone alcohol (DAA) was purchased from Sankyo Chemical Co., Ltd.

Table 1. Composition of negative photo-sensitive materials.

| Bank Color | Transparent | White | Black | Gray |
|------------|-------------|-------|-------|------|
| No.        | (a)         | (b)   | (c)   | (d)  |
| Polymer    | Siloxane Polymer | 35    | -     | 10   | 20  |
|            | Acrylic Polymer | -     | -     | 20   | 10  |
| Pigment    | TiO₂ Pigment | -     | 25    | -    | -   |
|            | Carbon Black Pigment | - | - | 5   | -   |
|            | UV-transparent Black Pigment | - | - | - | 5  |
| Additives  | Omnisil819   | 10    | 10    | 20   | 20  |
|            | Additives    | 4     | 3     | 3    | 3   |
| Solvent    | PGMEA        | 30    | 30    | 30   | 30  |
|            | DAA          | 20    | 20    | 20   | 20  |

(a) Transparent bank material with siloxane polymer. (b) Transparent bank material with acrylic polymer. (c) White bank material with siloxane polymer and TiO₂ pigment. (d) Black bank material with siloxane polymer and carbon black pigment. (e) Black bank material with siloxane polymer and UV-transparent black pigment. (f) Gray bank material with siloxane polymer, TiO₂ pigment and UV-transparent black pigment.

2.2. Patterning process
These materials were coated by a spin coater (MS-A100, Mikasa Co.) on each glass substrate to obtain 10 μm thickness after 230 °C curing.

The coated substrates were dried at 100Pa for 60 sec in a vacuum dryer (VCD; Micro Engineering Inc.) and baked at 90 °C for 180 sec on a hot plate (HPD-3000BZN, AZ One Co.).

The baked substrates were exposed by an aligner (g,h,i-line, PLA-501F, Canon Inc.) with 300 mJ/cm² (at 365nm) through a mask for grid-type banks (subpixel size: 300 μm×100 μm, line width: 20 μm) or without mask. Mask gap was 50 μm.

The exposed substrates were developed by 0.045% potassium hydroxide solution with a surfactant (KOH, AD-1200, Takizawa-sangyo Co.).

The developed substrates were post-baked at 230 °C for 30 min under an air atmosphere by using oven (DN43HI, Yamato scientific Co.) individually.

2.3. Evaluation
2.3.1. 1% weight loss temperature (TGA data)
1% weight loss temperature was measured by TGA (Thermogravimetric analyzer; TGA-50, SHIMADZU Co.).
2.3.2. Pattern profile, taper angle, and thickness
Pattern profiles of cured banks on glass substrates were observed by Scanning Electron Microscope (SEM; S-4800, Hitachi). Taper angle and thickness of banks were measured from the SEM image.

2.3.3. Transparency and OD value (light-shielding properties)
Transparency of the cured film (10 μm) was measured by a spectrometer (UV-4100, Hitachi High-Technologies Co., Ltd.). OD value of the cured film (10 μm) was calculated by the following equation.

\[
\text{OD value} = -\log_{10}\left(\frac{\text{Transparency of the cured film} \, \%T}{100}\right)
\]

2.3.4. L*, a*, b*, reflectivity
L*, a*, b*, and reflectivity of the cured film (10 μm) were measured in SCI mode by a split color meter (CM-2600d, KONICA MINOLTA).

3. Results and discussion
3.1. Heat resistance and patterning property
We investigated for the purpose of developing bank materials that combine patterning property, heat resistance, light-shielding property, and reflective property. We started to evaluate the heat resistance in the beginning, and subsequently evaluate the patterning property.

We prepared two kinds of transparent bank materials, material (a) and material (b), using siloxane polymer and acrylic polymer, respectively. We compared their heat resistance in order to select the base polymer. We measured 1% weight loss temperature of them by TGA measurement. The banks formed by material (a) showed at 350 °C, while the banks formed by material (b) at 288 °C (Table 2). This result indicates that the heat resistance of the material with siloxane polymer is higher than the one of the material with acrylic polymer. Then, we evaluated the patterning properties of them by SEM. We confirmed that material (a) could form transparent banks with a good taper angle of 88° at a thickness of 10 μm. Transparent banks formed by material (b) also have a good taper angle of 86° at a thickness of 10 μm (Table 2).

Next, we investigated to form colored banks using siloxane polymers in order to develop light-shielding banks with high reflectivity. We started developing white bank materials using TiO₂ pigment and siloxane polymer based on our conventional white material because of high reflectivity. By optimizing the composition, we succeeded in developing material (c) that could form white banks with a good taper angle of 87° at a thickness of 10 μm (Table 2).

Then, we tried to develop black bank materials for good light-shielding property by using carbon black pigment, which is one of the most commonly used black pigments. However, banks with an inverse taper angle of 120° were formed by material (d) using carbon black pigment (Table 2). This would be caused by the pigment absorbing the exposure light, and it was thought that the light did not reach the bottom of the film. To improve this light absorption, we used a black pigment that transmitted UV light instead of the pigment and formed black banks of material (e). As we expected, the banks had a thickness of 10 μm with a good taper angle of 87° (Table 2).

We set out to develop gray banks because we thought it is possible for them to achieve both properties of high light-shielding and high reflectivity, which are suitable for the QD-CF banks. Material (f) was successfully developed by optimizing the amount of TiO₂ pigment and the UV-transparent black pigment. This material could form gray banks with a good taper angle of 86° at a thickness of 10 μm (Table 2). The SEM and microscope images of the pattern are shown in Fig. 2.

We confirmed 1% weight loss temperature of these colored banks (white, black, and gray banks) by TGA measurement. All of the banks showed at over 288°C (Table 2). Figure 3 shows TGA data of gray banks formed by material (f) as an example. The 1% weight loss temperature was 353 °C. These results indicate that all of the banks with siloxane polymer had high heat resistance.

| No. | Transparent Bank Color | White | Black | Gray |
|-----|------------------------|-------|-------|------|
|     |                        | (a)   | (c)   | (d)  | (e)  | (f)  |
| 1% weight loss temperature (°C) | 350 | 288 | 353 | 348 | 348 | 353 |
| Thickness (μm) | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Taper angle (°) | 88 | 86 | 87 | 120 | 87 | 86 |
| Transparency (%T) @450nm | 91.6 | 90.5 | 9.60 | 0.12 | 0.13 | 0.63 |
| OD value @450nm | 0.04 | 0.04 | 1.02 | 2.90 | 2.89 | 2.20 |
| L* | 34.5 | 35.2 | 90.4 | 28.3 | 28.3 | 76.3 |
| a* | 0 | -0.1 | -2.5 | 0.5 | 0.5 | -0.5 |
| b* | -0.4 | -0.5 | -1.3 | 0.4 | 0.4 | 1.8 |
| Reflectivity (%T) @550nm | 7.5 | 8.5 | 77.7 | 5.2 | 5.3 | 50.8 |

Table 2. Cured film properties.
3.2. Light-shielding and reflective properties

Furthermore, we evaluated light-shielding and reflective properties of the formed banks.

We compared the light-shielding properties of them by measuring the transparency at a wavelength of 450 nm (blue light). The results are summarized in Table 2. The transparent and white banks were found to be unsuitable for QD-CF banks because the transparency exceeded 5%. On the other hand, the black and gray banks had a transparency of less than 1%. The OD (optical density) values of them exceeded 2.0 per 10 μm. These results showed that the black and gray banks had good light-shielding property. Transparency graphs of the white, black, and gray banks are shown in Fig. 4.

Finally, we compared the reflective properties of the banks by measuring their reflectivity at a wavelength of 550 nm. The results are summarized in Table 2. The reflectivity of the transparent and black banks were less than 10%. On the contrary, the white and gray banks showed high reflectivity of over 50%. Transparency graphs of the white, black, and gray banks are shown in Fig. 5.

These results showed that the obtained gray bank was found to be the most suitable for QD-CF display because the bank had both good light-shielding property and high reflectivity.

4. Conclusion

We confirmed that the combined use of TiO₂ pigment and UV transparent black pigment could afford gray banks with a good taper angle of 86° at a thickness of 10 μm. The gray banks showed good light-shielding property (transparency at 450 nm<1%), high reflectivity of 50.8% at 550 nm, and high heat resistance (1% weight loss temperature is 353 °C). This developed material is ideal for application of QD-CF display. We will fill QD materials between the banks and verify their optical properties in the near future.

References

1. K. H. Kim and J. K. Song, NPG Asia Mater., 1 (2009) 29.
2. H. W. Chen, J. H. Lee, B. Y. Lin, S. Chen, and S. T. Wu, Light Sci. Appl., 7 (2018) 17168.
3. N. Koma, M. Hashizume, H. Kato, T. Ishinabe, and H. Fujikake, SID Int. Symp. Dig. Technol., 49 (2018) 1660.
4. Y. C. Shi and F. G. Shi, *IEEE J. Sel. Top. Quantum Electr.*, 23 (2017) 1901304.
5. H. W. Chen, J. He, and S. T. Wu, *IEEE J. Sel. Top. Quantum Electr.*, 23 (2017) 1900611.
6. M. Suwa, T. Fujiwara, T. Okazawa, and H. Araki, *J. Photopolym. Sci. Technol.*, 24 (2011) 259.
7. T. Okazawa, K. Ono, and M. Suwa, *J. Photopolym. Sci. Technol.*, 25 (2012) 349.