Transitional analysis of organic thin color filter layers in displays during baking process using multi-speckle diffusing wave spectroscopy

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The color filter (CF) is one of the key components for improving the performance of TV displays such as liquid crystal display (LCD) and white organic light emitting diodes (WOLED). The profile defects like undercut during the fine fabrication processes for CF layers are inevitably generated through the UV exposure and development processes, however, these can be controlled through the baking process. In order to resolve the profile defects of CF layers, in this study, the real-time dynamic changes of CF layers are monitored during the baking process by changing components such as polymeric binder and acrylate. The motion of pigment particles in CF layers during baking is quantitatively interpreted using multi-speckle diffusing wave spectroscopy (MSDWS), in terms of the autocorrelation function and the characteristic time of α-relaxation.

Keywords: multi-speckle diffusing wave spectroscopy, undercut, CF layer, baking process, rheology, displays

1. Introduction

There are several important issues in display industries; a bright screen with low energy consumption (Chu et al., 2007; Han et al., 2012), excellent image resolution such as ultra-high definition (UHD) and high color gamut (Kunić and Šego, 2013; Mentley, 2002), and three-dimensional (3D) images. Research development for minimizing pixels in display panels and improving aperture ratio is also in significant progress. These needs depend on stepwise-increasing pattern resolution and better overlap accuracy and pitch control. Various structural characteristics of display panels are largely determined by the photolithography operation in the panel manufacturing processes.

As the size of TV display panels has expanded to 65 inches and further 71 inches, the size of substrates has simultaneously increased more than 75 times from one generation (300 × 400 mm) in the 1990s to now ten generation (2,880 × 3,130 mm). Process quality control should be naturally required for the technology advancement to increase the substrate size without defects. For example, a key issue is to improve the illumination performance of displays maintaining the critical dimension (CD) with proper sidewall profile of color filter (CF) layers. CD means the width and length of a patterned structure on a pixel. However, the process for producing fine and uniform CF layers arouses various structural defects.

One representative problem is a side wall profile defect of CF layers, called an undercut, mainly occurring in their fine fabrication processes (Park et al., 2012; Park et al., 2017). The bottom part of CF layer undesirably caves in Fig. 1, triggering the disconnection of upper indium tin oxide (ITO) layers (Park et al., 2012). The undercut is critically influenced by the combined effects of UV exposure, development, and baking processes in the photolithography operation. Figure 1 shows the schematic change in a CF layer profile during the manufacturing processes. In general, an undercut inevitably occurs due to non-uniform crosslinking density during UV exposure process for CF layers, as delineated in Fig. 2, resulting in overly dissolving at the side-bottom of CF layer in the development process and then melting in the baking process (Park et al., 2017).

Figure 2a shows the typical manufacturing processes with several stages for producing CF layers, based on a pigment method using a color photoresist (Kudo et al., 1998; Sabnis, 1999; Tsuda, 1993; Yen and Tso, 2004). First, a black matrix for blocking light is formed and then a color photoresist for CF layers is coated on a glass substrate. Next, a UV exposure process for making an insoluble layer and a development process for removing an unnecessary portion by a developer (e.g., 1 wt.% KOH aqueous solution) are carried out. Finally, CF layers are produced with proper physical properties through a baking process. The red-green-blue (RGB) layers are fabricated by repeating the above steps and then ITO layers are coated on RGB layers. When manufacturing large-area...
panels such as TV displays, the proximity UV exposure process is the standard for CF layers because it provides sufficient resolution and overlay control capability (Lin et al., 2012). Light passes through a slit and air gap between the photomask and the photoresist (Kudo et al., 1998; Lin et al., 2012; Park et al., 2012; Park et al., 2017; Sabnis, 1999; Tsuda, 1993; Yen and Tso, 2004). The important factors in manipulating crosslinking density and profile change of CF layers are the distribution of light intensity by Fresnel diffraction (Chuang et al., 2002; Lin et al., 2012) at the slit edge and the control of air gap. The light intensity passing through the photomask slit is unavoidably diminished at the side by Fresnel diffraction; the narrower the slit width, the lower the intensity distribution. Also, since the light is absorbed or scattered at a photoresist, the crosslinking capability at the bottom of photo-

Fig. 1. (Color online) The change of CF layer profile during the manufacturing processes.

Fig. 2. (Color online) The manufacturing processes for CF layers and light diffraction at the mask slit.
resist is relatively small owing to the decreased exposure light in the range of 365-436 nm during the UV exposure process (Kudo et al., 1998). It is generally known that the intensity reduction by diffraction can be alleviated by reducing the air gap (Chuang et al., 2002; Lin et al., 2012). However, there exists a limit to extremely reduce the air gap, considering the contact with the photoresist that leads to the photomask deflection.

Several studies have introduced meaningful materials and process parameters including resist thickness, exposure dose, and air gap to control the photoresist profile in the proximity photolithography processes (Loechel et al., 1996; Park et al., 2012; Sabnis, 1999; Tsuda, 1993). Chuang et al. (2002) effectively removed the light diffraction using materials optimized to air gaps during the UV exposure process. Park et al. (2012) investigated the effect of the air gap and exposure dose on the wall profile of CF layers in the UV exposure process. However, there have been few attempts to correlate the pigment dynamics and profile changes of CF layers during the baking process, where the pattern shape of CF layers is finally transformed. The baking process is operated in a temperature range of about 130-250°C for 10-30 min to remove the solvent and moisture residues, modify the morphology, and reinforce the photoresist against physical/chemical etching in subsequent processes. Therefore, the quantitative analysis of the rheological properties of CF layers during baking process is very crucial to suitably handle the undercut phenomenon.

In this study, real-time dynamic changes of CF layers with undercut defect during the baking process were systematically characterized, using a non-contact light scattering method called multi-speckle diffusing wave spectroscopy (MSDWS) (Bellour et al., 2003; Brunel et al., 2007; Cohen-Addad and Hohler, 2001; Knaebel et al., 2000; Lee et al., 2013; Narita et al., 2004; Oh et al., 2017; Park et al., 2017; Viasnoff et al., 2002; Viasnoff et al., 2003). MSDWS consists of a laser unit (Jinsung Laser, DPGL-2200, Korea) with a 532 nm wavelength and 1mm beam diameter (beam mode of TEM00), several mirrors, and a multi-speckle detector such as a CCD camera or a line scan camera (Lee et al., 2013). This equipment is useful for quantitatively measuring changes in particle movements under non-ergodic conditions, such as a baking process or a suspension drying. Employing MSDWS, the light intensity scattered by the motion of pigment particles in CF layers and changeable refractive index of the photoresist was monitored in real-time during the baking process for evaluating autocorrelation function and characteristic time (e.g., α-relaxation time (Narita et al., 2004; Oh et al., 2017; Park et al., 2017)). Pigment particles are mainly agglomerated into clusters of various sizes within CF layers through the drying process. During the baking process, the polymer material containing pigment clusters melts and pigment particles tend to migrate, affecting speckle images. The undercut was also interpreted by the rheological behavior of the photoresist for CF layers during the baking process.

2. Experimental Details

2.1. Preparation of color photoresist for CF layers

Negative-type photoresists were prepared by mixing a polymer binder (Mw 5,000 or 10,000 g/mol, Miwon, Korea), a polyfunctional acrylate (DPHA or DPCA-20, Nippon Kayaku, Japan; see Fig. 3 for their structures), green pigment (DIC, Japan), photoinitiators (I-907, Ciba, Japan and OXE 01, BASF, Germany), solvent (propylene glycol monomethyl ether acetate (PGMEA)), and a surfactant (F-475, DIC, Japan) at room temperature for 6 h. Note that negative-type photoresists are more stable and reliable for their crosslinking and polymerization than positive-type ones. They were then filtered through a 2 μm filter. The detailed information of components is listed in Table 1. Three samples were prepared by changing the combination of binder resin and acrylate; DPHA-10k, DPCA-20-10k, and DPHA-5k.

2.2. Fourier transform infrared (FTIR) analysis of CF layers in manufacturing process

Thin CF layers for evaluating the UV curing reaction were fabricated under the actual manufacturing conditions. The photoresist was coated on a transparent glass
Table 1. Formulation of color photoresist samples for Green CF layers.

<table>
<thead>
<tr>
<th></th>
<th>Sample 1:</th>
<th>Sample 2:</th>
<th>Sample 3:</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DPHA-10k</td>
<td>DPCA-20-10k</td>
<td>DPHA-5k</td>
<td></td>
</tr>
<tr>
<td>Binder resin</td>
<td>Acrylic binder</td>
<td>Acrylic binder</td>
<td>Acrylic binder</td>
<td>8</td>
</tr>
<tr>
<td>Mw</td>
<td>10,000</td>
<td>10,000</td>
<td>5,000</td>
<td></td>
</tr>
<tr>
<td>Pigment</td>
<td>Green 35</td>
<td>DPCA 20**</td>
<td>DPHA</td>
<td>15</td>
</tr>
<tr>
<td>Polyfunctional acrylate</td>
<td>DPHA*</td>
<td>DPCA 20**</td>
<td>DPHA</td>
<td>4</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>OXE 01 &amp; Irgacure 907</td>
<td></td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>PGMEA***</td>
<td></td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>Additive</td>
<td>Fluoro surfactant (F-475)</td>
<td></td>
<td>0.2</td>
<td></td>
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<tr>
<td>Total</td>
<td></td>
<td></td>
<td>100</td>
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DPHA* = Dipenta-erythritolhexa-acrylate  
DPCA 20** = DPHA ε-caprolactone adduct  
PGMEA*** = Propylene glycol monomethyl ether acetate

substrate, followed by vacuum drying and oven drying at 90°C for 1 min. The CF layers of 10 mm CD and 2.3 μm thickness were produced using a developer (1 wt.% KOH) in the development process. In the process of manufacturing CF layers, the UV curing reaction involving the C=C double bonds in the acrylate (DPHA or DPCA-20) was analyzed by FT-IR (Aramis IR2, Horiba, Japan) and expressed in the degree of conversion (DC). DC of reacted samples was determined by the ratio of C=C bonds at 1637 cm⁻¹, based on the unreacted C=O bonds at 1730 cm⁻¹, before UV exposure and after UV exposure (400 mJ/cm²) and thermal baking for 20 min. DC was calculated from the equivalent ratio of cured (C) and uncured (U) samples, as shown in Eq. (1):

\[
DC (\%) = 1 - \left(\frac{C}{U}\right) \times 100%.
\]  

2.3. Rheological measurement of thick CF Layers in the baking process

Somewhat thick CF layers (250 μm), based on a baking process, were prepared to measure their bulk rheological properties. CF layers were coated on a separable film, dried at 90°C for 2 min, and then trimmed into a disc-shaped film of 9 mm diameter. Specimens were irradiated by UV (2.8 J/cm²) at room temperature and then trimmed into a disc-shaped film of 9 mm diameter. Specimens were irradiated by UV (2.8 J/cm²) before UV exposure and after UV exposure (400 mJ/cm²) and thermal baking for 20 min. DC was calculated from the equivalent ratio of cured (C) and uncured (U) samples, as shown in Eq. (1):

\[
DC (\%) = 1 - \left(\frac{C}{U}\right) \times 100%.
\]  

2.4. Non-contact measurement of actual thin CF layers in the baking process

Thin CF layers for analyzing the dynamic melting behavior were fabricated under the actual manufacturing conditions. The photoresist was coated on a transparent glass substrate, followed by vacuum drying and oven drying at 90°C for 1 min. After the irradiation (400 mJ/cm²) through the UV exposure process, the CF layers of 100 μm CD and 2.3 μm thickness were produced using a developer (1 wt.% KOH) in the development process. The speckle images of the prepared specimens were obtained using a charge coupled device (CCD) camera in MSDWS. A green laser with a wavelength of 532 nm and a beam diameter of 1 mm was used in the experiment. A low output power of 15 mW was applied to minimize the temperature change of the specimen by light. The detailed information of MSDWS was presented in previous studies (Lee et al., 2013; Oh et al., 2017; Park et al., 2017). Dynamic changes of CF layers during the baking process were quantified by autocorrelation functions evaluated from scattered images by pigment particles under constant temperature conditions of 60, 100, and 200°C and dynamic temperature conditions in the range of 30°C to 200°C.

Autocorrelation function between initial measuring time \(t_1\) and lag time \(\tau\) is expressed as follows (Bellour et al., 2003; Cohen-Addad and Hohler, 2001; Knaebel et al., 2000; Lee et al., 2013; Narita et al., 2004; Park et al., 2017; Viasnoff et al., 2002):

\[
g_{2}(\tau) = 1 - \frac{\langle I_n(t_1 + \tau)I_n(t_1) \rangle_n - \langle I_n(t_1) \rangle_n^2 \langle I_n(t_1 + \tau) \rangle_n^2}{\langle I_n(t_1 + \tau) \rangle_n^2 \langle I_n(t_1) \rangle_n^2}\]

where \(g_{2}(\tau)\) denotes the autocorrelation function, \(I_n\) is the light intensity at the \(n\)th pixel, \(\langle \cdots \rangle_n\) is the ensemble average over the pixels, \(t_1\) is the initial measuring time, and \(\tau\) is the lag time relative to \(t_1\). The autocorrelation function, \(g_{2}(\tau)\), representing the correlation level between the light intensities at two different times, is obtained by ensemble averaging of \(n\) speckles. The lag time from the initial measuring time was within 100 s.

During the baking process, the profile changes of thin
CF layers were also observed directly using a scanning electron microscope (SEM, Vega SE, TESCAN, USA) at baking times 2 and 20 min within a chamber at 200°C.

3. Results and Discussion

3.1. Degree of conversion of CF layers in the manufacturing processes

In negative-type photoresist for making CF layers, the binder polymer and the acrylate monomer are crosslinked via radical polymerization during the UV exposure process. Figure 4 portrays the schematic crosslinking reaction of a photoresist during the UV exposure and baking processes. The unreacted parts in a photoresist during the UV exposure process are dissolved by the developer and subsequently rinsed off with water in the development process. The unreacted photoresist, which is not dissolved, however, is further melted and cured in the subsequent baking process to form a stable and patterned structure on a glass substrate. The IR absorbance data of DPHA-10k CF layer before the UV exposure and after the UV exposure and thermal baking were measured to qualitatively figure out the conversion of C=C double bonds in the acrylate. Figure 5a represents the peaks of IR vibrations of the C=C double bonds at 1637 cm\(^{-1}\) based on those of the unreacted groups, C=O, at 1730 cm\(^{-1}\). C=C double bonds were considerably reduced in the FT-IR spectra (Fig. 5b) after UV exposure and thermal baking in comparison to the case before UV exposure, demonstrating the polymerization reaction in polyfunctional acrylates. It is found that DC by Eq. (1) increased to 38% just after the UV exposure and further increased to about 79% after the UV exposure and thermal baking, confirming the crosslinking mechanism in Fig. 4. From these results, the polymer melted in the baking process reinforced the curing to finally form CF layers through more active free-radical reaction. The melting step of baking process plays an important role in tuning the melt properties and controlling the profile defects of CF layers.

3.2. Rheological changes of thick CF films

Melting and curing features of thick CF layers during the baking process were analyzed indirectly through rhe-
ological measurements under dynamic temperature condition. Note that this test cannot fully support the rheological characteristics of actual thin CF layers of a few micron thickness. The complex viscosities, $\eta^*$, of thick CF films produced from three samples are compared in Fig. 6. It is meaningful to compare viscosity changes of CF films along temperature to intuitively estimate the profile change of CF layers during the baking process. Viscosities of thick CF layers decreased in the temperature range from 40°C to 195°C and tended to rapidly increase above 195°C. In the viscosity-decreasing region, the fluidity of CF layers rises by thermal melting of components. In the rapid viscosity-increasing region above 195°C, the hardness of CF layers is sharply enhanced because of the subsequent curing of components. In particular, the viscosity of CF layers by DPHA-10k sample increased below 170°C in comparison to others. Viscosity level of DPHA-5k sample is the lowest in all temperature ranges, implying that the low molecular weight of acrylic binder resulted in the higher fluidity of CF layers under the given temperature condition.

3.3. Dynamic pigment motions in CF layers during the baking process

The speckle images scattered on thin CF layers by MSDWS are due to the dynamic movement of pigment particles in CF layers during the baking process. Figures 7a-7c show the autocorrelation function ($g_2-1$) data of thin CF layers measured at several constant temperatures (60°C, 100°C, and 200°C). The fast decrease of the autocorrelation function curve means that the correlation of speckle images between $t_w$ and $t_w + \tau$ rapidly vanished and

![Fig. 6. (Color online) Rheological properties of thick CF films along the measuring temperature from 30 to 200°C.](image)

![Fig. 7. (Color online) Autocorrelation functions of three CF layers under different baking temperature conditions: (a) 60°C, (b) 100°C, and (c) 200°C. (d) Characteristic times for $\alpha$-relaxation of CF layers.](image)
the movement of pigment particles was very active due to the melting of CF layers. The autocorrelation function decreased faster as the temperature increased from 60°C to 200°C, making the fluidity of CF layers increase. The changes in autocorrelation function of CF layers at each temperature condition could be quantified by a characteristic time called $\alpha$-relaxation. The $\alpha$-relaxation is associated with the slow motion such as particle rearrangement (Narita et al., 2004; Oh et al., 2017; Park et al., 2017). As in previous cases (Oh et al., 2017; Park et al., 2017), the characteristic time for $\alpha$-relaxation is defined as the time when the autocorrelation function decreases to 0.6. It was also verified that the characteristic time can be used to effectively quantify the change in fluidity of CF layers.

Figure 7d shows the characteristic times for thin CF layers at several temperatures. The CF layer produced by DPHA-10k exhibited longer characteristic time than others because the particle movement in this CF layer with higher viscous feature was relatively low. The CF layer by DPHA-5k showed shorter characteristic time in all temperature ranges and also DPCA-20-10k contributed to the reduction of the characteristic time in comparison to the DPHA-10k case with the same molecular weight binder. Figures 8a-8c display the changes in autocorrelation function ($g_2(\tau)$) data during a lag time of 100 s for several CF layers measured during the initial baking process (i.e., temperature change from 30°C to 200°C for 2 min). Analysis of autocorrelation function with increasing temperature is very suitable to figure out the pigment movement in CF layers during the baking process. The autocorrelation function rapidly decreased along the lag time in the initial baking because the correlation between particles with active motions in CF layers abruptly disappeared. Thereafter, a gradual increase in the autocorrelation function curve was observed along the lag time with further increasing baking time.

Figure 8d shows the average $\alpha$-relaxation behavior of CF layers with baking time in the initial baking process, based on the results of Figs. 8a-8c. In all experimental sets, the characteristic time of $\alpha$-relaxation decreased momentarily until 10 s and then maintained a low level. The initial decrease of characteristic time suggests that the fluidity of CF layers was enhanced by the thermal melting, showing the similar behavior as in Fig. 6 for complex viscosities of thick CF films.

The temperature-dependent fluidity of thin CF layers could be effectively detected by the non-contact MSDWS. Specifically, the CF layer by DPHA-10k maintained the...
longest characteristic time in the beginning of the baking process. In the case of DPCA-20-10k, similar fluidity was observed up to 80°C as in the DPHA-10k case, however, its characteristic time over 80°C is lower than that of DPHA-10k. The CF layer by DPHA-5k retained the shortest characteristic time in the initial baking step due to the increased fluidity of this layer with low molecular weight acrylic binder.

3.4. Profile changes of CF layers in the baking process

In order to visualize the profile changes of CF layers caused by their different fluidity during the baking process, as in Fig. 9, the SEM cross-sectional images of CF layers before and after the baking process were captured at different baking times (i.e., 0, 2, and 20 min) under 200°C. The shape of CF layer by DPHA-5k (Fig. 9c), which showed the shortest characteristic time in the initial baking process, remarkably changed within the initial 2 min, substantiating that the undercut CF layer was effectively healed at the initial stage. On the other hand, the DPHA-10k case (Fig. 9a) with the longest characteristic time was not fully recovered from the undercut state at initial 2 min and even 20 min baking times. In the case of DPCA-20-10k (Fig. 9b) with the moderate characteristic time, the undercut was fairly healed in comparison to the DPHA-10k case, although the shape was not completely recovered. It will be very important to investigate the fluidity of CF layers within the initial baking time of 2 min in order to control the shape defect of CF layers. The application of MSDWS, a real-time non-contact method, provides meaningful information on the relation between the fluidity of thin CF layers and shape defects in the baking process.

4. Conclusions

The wall profile defects of CF layers such as undercut, which inevitably occurred in the photolithography processes, were examined, employing MSDWS which is a non-contact light scattering method, for the real-time measurement of dynamic changes of pigment particles in CF layers during the baking process with both thermal melting and thermal curing. This defect is dependent on the crosslinking density at the layer side and melting charac-

![Fig. 9. Profile changes of CF layers ((a) DPHA-10k, (b) DPCA-20-10k, and (c) DPHA-5k) during the baking process.](image-url)
teristics of a CF layer. Effect of components such as polymeric binder and acrylate on the rheological properties and dynamic changes of CF layers during the baking process was mainly focused on this study. Movement of pigment particles in CF layers in the baking process was evaluated in terms of the autocorrelation function and the characteristic time (i.e., $\alpha$-relaxation time). In the initial baking process, CF layers with different components showed different pigment motions, which were closely related to their fluidic features. Undercut shape for a CF layer with low molecular weight was favorably healed within the initial baking time of 2 min. MSDWS is a useful tool to effectively address dynamic changes of CF layers with an undercut in the baking process.

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