Materials Research Express

PAPER

Mobile ion induced electric field effect in polymer-stabilized vertical alignment liquid crystal display

To cite this article: Nakcho Choi *et al* 2018 *Mater. Res. Express* **5** 095312

IOP Publishing Mater. Res. Express 5 (2018) 095312 https://doi.org/10.1088/2053-1591/aad992

Materials Research Express

CrossMark

RECEIVED
14 June 2018

REVISED
2 August 2018

ACCEPTED FOR PUBLICATION
10 August 2018

PUBLISHED
20 August 2018

PAPER

Mobile ion induced electric field effect in polymer-stabilized vertical alignment liquid crystal display

Nakcho Choi[1,2], Jonghak Hwang[1], Dongil Yoo[1], Yongwoo Lee[1], Yeogeon Yoon[1], Byoungho Cheong[2] and MunPyo Hong[2]

[1] Display Research Center, Samsung Display Co. Ltd, 1 Samsung-ro Giheung-gu Yongin-si Gyeonggi-Do 17113, Korea
[2] Department of Applied Physics, Korea University, 2511 Sejong-ro Sejong-si 30019, Korea

E-mail: goodmoon@korea.ac.kr

Keywords: mobile ion, liquid crystal, display, PS-VA

Abstract

Mechanisms of radical polymerization on the surface of the alignment layer in polymer stabilized vertical alignment (PS-VA) liquid crystal display (LCD)are suggested. When DC voltage is applied between top and bottom electrode, it is observed that the liquid crystal molecules distort alignment directions, which deteriorate luminance uniformity during UV irradiation process. It is revealed that the liquid crystal movement is attributed to mobile ions, (K^+, OH^-), smearing out from the interface at the lower layer of the pixel electrode. The mobile ions are generated from the developer remains after color filter formation process. To minimize the influence of the mobile ions, the thickness of the insulating SiNx layer under the pixel electrode and the color filter is increased, which contribute to luminance reduction rate from 20% to less than 1%.

1. Introduction

PS-VA LCD is known to be a display with high contrast ratio (CR), high brightness, and fast response time [1–6]. Since there are non-patterned top plate electrode and micro-slit shaped bottom electrode in the PS-VA LCD, liquid crystal molecules are normally aligned to the slit directions so that it has high aperture ratio compared with patterned vertically alignment (PVA) mode. Fast response is achieved by forming pretilt angle of liquid crystal, being controlled by adding a small amount of reactive monomers in liquid crystal. The liquid crystal is tilted by UV light polymerization process under the DC voltage [7–10]. But there has not been many studies on the mechanism of pretilt formation process on the surface of the alignment film. Lyu and coworkers suggested that the PS-VA's phase separation is attributed to an isotropic separation rather than anisotropic phase separation composite film [11–13]. Phenomenologically, in the PS-VA mode, the monomer in the liquid crystal seems to migrate to the top and the bottom of alignment before UV irradiation, and is polymerized by UV irradiation, resulting in the protrusion at top and bottom of the alignment layer. The initial pretilt angle is not uniform on the surface of the alignment film, which often causes degradation of display quality. To keep the pretilt angle stable, it is necessary to irradiate additional UV irradiation long enough to remove residual monomers without applying voltage. However, it is still not clear what makes the misalignment of liquid crystal and how to control the pretilt angle.

In this paper, we suggest the abnormal pretilt angle is mainly formed by charged mobile ions at the interface layer under the electrode. The ion impurities could be originated from various substances such as liquid crystal, alignment layer, organic layer, cleaning agent, and so on. We verified the correlation between the amount of mobile ions in the interface and the abnormal liquid crystal texture by experiments and simulations. It is suggested that the influence of the electric field generated by the mobile ions could be minimized by controlling blocking layer thickness.

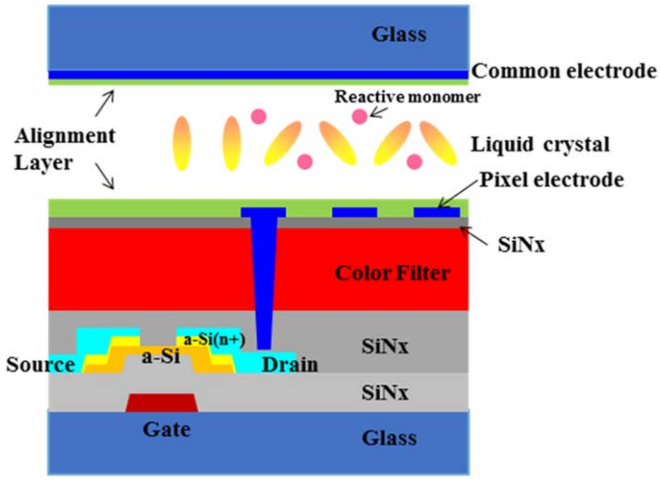

Figure 1. The schematic plots of cross section of pixel.

2. Experimental

Figure 1 shows schematic representations of vertical cross section and top view of PS-VA LCD panel. After thin film transistors were fabricated on glass substrate, color filters were formed through photolithography process. Then amorphous SiNx with thickness from 500 Å to 2500 Å was prepared using a parallel plate plasma-enhanced chemical vapor deposition (PECVD) systems at 200 °C and amorphous indium zinc oxide(IZO) with the thickness of 550 Å for pixel electrode was sputtered on the SiNx film. The electrodes were patterned as a fishbone shape. In the photo-resist patterning step, a micro-slit mask was used and the electrodes were etched using a wet etching process. The top-side glass was coated with IZO without patterning and the two glass layers were coated with polyimide (JSR Al-60702) as an alignment layer. The liquid crystals from Merck ($\Delta\varepsilon = -3.0$, $\Delta n = 0.1$) containing monomer in an amount of 0.2 wt% were injected into the cell, followed by the top and bottom glass sealed with UV curable sealant. The line and space width of the micro slit were 3 μm and 3 μm, respectively. This micro slit pattern makes the orientation of the liquid crystals in an applied electric vertical field align parallel to the slit direction in figure 2. To create the pretilt angle of the liquid crystals on the surface, the cell is irradiated with 5J of UV light with applying DC 5 V to the cell. The optical retardation was measured using the Axo-step 20H (Axometrics Inc.) and pixel luminance was measured with the BM-7A (Topcon Techno house Corp.). The surface of the cell was measured by the XE-100 EFM measurement (Park systems). To verify the mobile effect in PS-VA cell, we used Techwiz 3D simulator (SANAYI Systems Co., Ltd). We also analyzed the ion impurities by TOF-SIMS 5-100 (Ion-TOF gmbh.).

3. Results and discussions

3.1. Pretilt formation mechanism in PS-VA

Table 1 shows how the reactive monomer in the liquid crystal is polymerized on the surface of the alignment film during UV irradiation. The first step is monomer change to radical ions by the UV irradiation. In order for the monomer to undergo a radical reaction in the absence of radical initiator, a glass substrate should be fully covered with the liquid crystal. If UV is irradiated on the liquid crystal containing the monomer exposed in the air, the monomer does not change to radical because oxygen will terminate the radical reaction as an inhibitor. In the second step, radicals can undergo three processes. Free radicals interact with each other around the surrounding radicals so inactive molecule are formed. However, more radical chain reactions occur. Therefore, the free radicals have more chance to meet the reactive monomer. In other cases, a radical reaction takes place around the alignment film, which then reacts with the backbone of the polyimide alignment film and the chain reaction will occur. In this time, polymer protrusion is made. In the third step, as the concentration of monomer near the alignment film decreases, monomers in bulk diffuse to alignment layer. And then, the polymer reaction occurs in a chain reaction near the alignment layer.

The pretilt angle is formed when the liquid crystal near the alignment film is tilted by the electric field and a polymer protrusion is formed around the liquid crystal, the state of the tilted liquid crystal is fixed. The pretilt angle on the surface of the alignment film depends on the magnitude of the UV irradiation amount, the applied voltage, and the amount of reactive monomer. With the conditions of 0.2 wt% monomer and being increasing

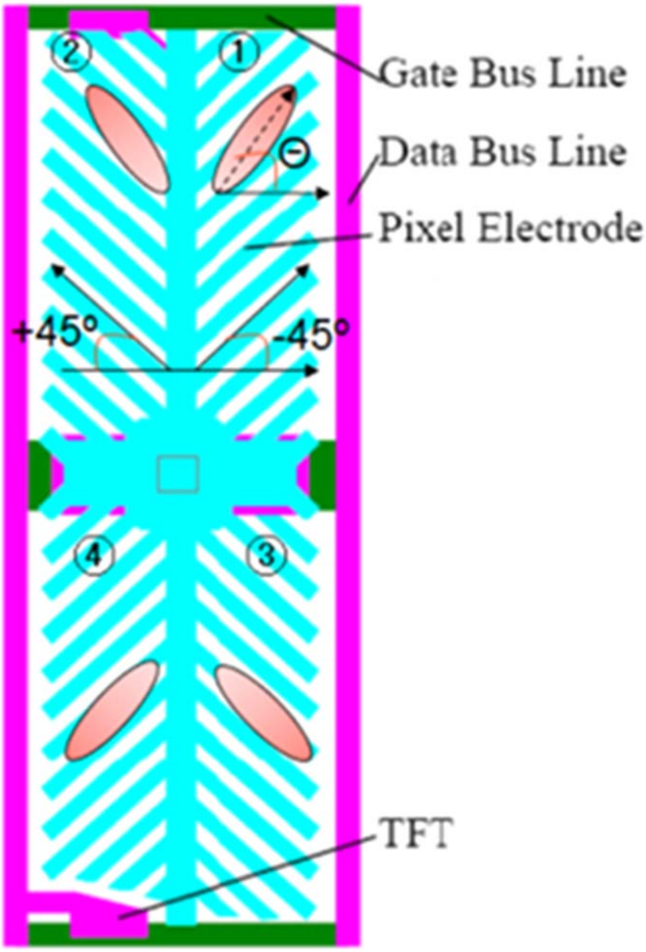

Figure 2. The schematic plots top view of PS-VA mode.

Table 1. Chemical reaction steps for reactive monomer being polymerized in PS-VA mode.

Step	Reaction
1	$M \rightarrow M^*$ (in the presence of UV light)
2	$M^* + M^* \rightarrow MM$
	$M^* + M \rightarrow MM^*, MM^* + M \rightarrow MMM^* \ldots$
	$M^* + Al. \rightarrow Al\text{-}M^*$
3	M^* diffuse to surface
4	$M + Al\text{-}M^* \rightarrow PI\text{-}MM^*, PI\text{-}MM^* + M \rightarrow PI\text{-}MMM^* \ldots$

(M : monomer, M^* : radical, PI : polyimide alignment layer).

voltage at the same UV intensity, the pretilt angle decreases, and being increasing the UV intensity at the same voltage, the pretilt angle also decreases. The pretilt angle of the liquid crystal is usually defined as the polar angle, θ and azimuthal angle, φ. The transmission axis of the polarizing plate is placed at 0 degree.

In PS-VA mode, it is known that the transmittance efficiency is determined as how much the liquid crystal is aligned to the direction of the micro slit electrode, while the black luminance depends on the pretilt angle in the polar direction [14]. The degree of orientation of liquid crystal can be expressed as slit direction ordering index (SOI) as in equation (1), where SOI is a statistical value indicating how the liquid crystals are aligned in the direction of the micro slit on average [15].

$$\mathrm{SOI} = \frac{\sum_{i=1}^{4} \mathrm{SOI_i}}{4}, \quad \mathrm{SOI_i} = \frac{1}{2}\left[\left\{\frac{3\sum_{n=1}^{k} \cos^2(\varnothing_n \pm_i 45)}{k}\right\} - 1\right] \tag{1}$$

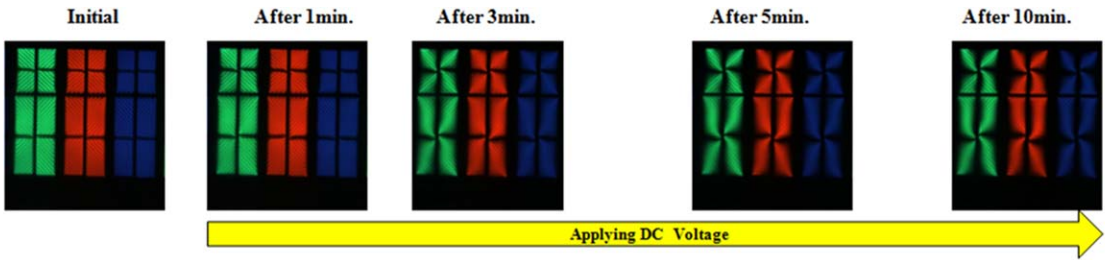

Figure 3. Optical polarizer microscopic images of a pixel under UV irradiation. The abnormal liquid crystal textures are shown as time increases.

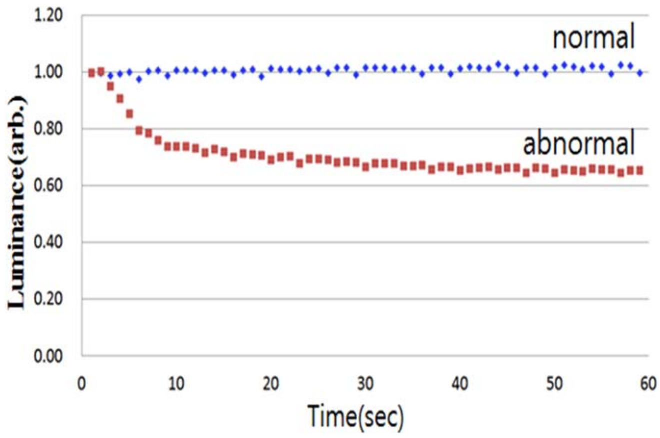

Figure 4. Comparisons of luminance curves of the normal and the abnormal panel, during the UV irradiation process while applying voltage.

where i, n and k means quadrant number of each pixel domains, nth liquid crystal and total number of liquid crystals in each quadrant domain area. $\pm$i means '+' in i = 1, 3, and '−' in i = 2, 4. Φn refers to azimuthal angle of *n*th liquid crysal. Pretilt angle and SOI value of liquid crystal are examined according to various applied voltages and UV irradiation energy.

3.2. Abnormal behaviour of liquid crystal during UV irradiation

The UV irradiation to liquid crystals while applying DCvoltage is very important process because it determines the pretilt angle, which is a major parameter controlling the contrast ratio and the transmittance of display. However, it has been found that there happens an abnormal behavior during UV irradiation, where the SOI value of the liquid crystal could not be stable during the UV irradiation, but it became smaller. In this case, the widths of the black brush lines were widened as shown in figure 3. When the DC voltage is 5 V, the luminance curve also decreases about 60% of normal state after 1 min, as shown in figure 4. However, when AC 5 V was applied, the luminance did not decrease as in the case of the normal curve. We assumed that is caused by the mobile ions near electrodes.

3.2.1. Electrostatic force microscopy

To verify the effects of mobile ions at the interface between the pixel electrode and the lower layer, the images of electrostatic force microscope (EFM) and atomic force microscope (AFM) were performed [16]. Figure 5(a) shows an AFM image of IZO electrodes, which are patterned with micro-slit shape on SiNx layers. It clearly shows the IZO electrodes are represented as bump shape. However, for the same pattern, EFM measurement (figure 5(b)), revealed that the SiNx surfaces are shown as bump, which means that the surface of SiNx is positively charged compared to the IZO electrodes.

The results of SOI measurement which was done by Axo-step 20H are compared with those of EFM measurement for normal and abnormal panels in figure 6. The SOI value of the abnormal panel is lowered by over 10% than that of normal panel and the surface voltage level in EFM measurement, which is attributed to the charge density on surface are higher over 20% than the normal panel. Therefore, we conclude that the abnormal panel has many mobile ions in bottom layer. In fabrication processes, the color filter layers are located under

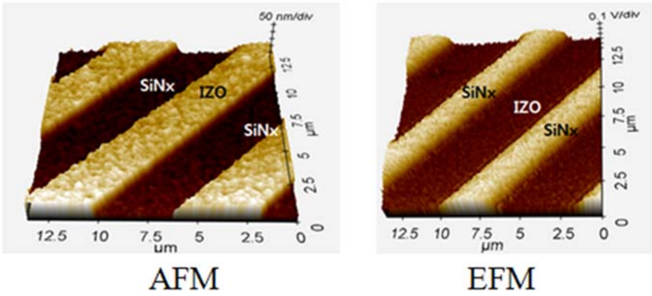

Figure 5. AFM and EFM images of patterned IZO on SiNx.

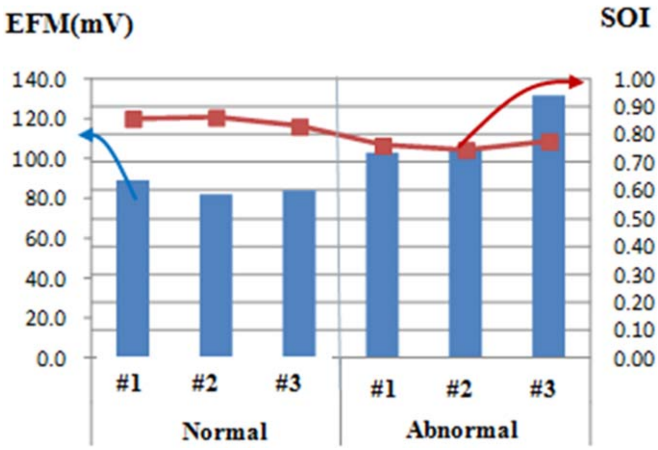

Figure 6. Surface voltage measured by EFM and SOI values of normal panel and abnormal panel.

SiNx. During the photo lithography and the cleaning process, the developer KOH solution is usually used for each red, green and blue color filter. We estimated that the developer or cleaning solution used during this development process might be the source of the mobile ions.

3.2.2. Verifications of mobile ion sources

To verify the mobile ion effect, two panels are prepared with different color filter processes. One is prepared for using only red photo-register(PR) as a color filter material, followed by the PR coating, exposure, development, and curing steps. The other one is prepared through the same process in that only red PR is used, but the panel is intentionally added green and blue PR coating, development, and curing process. In this case, it is noted that the exposure processes of green and blue PR are skipped so that the two of PRs are easily removed. The only difference between the two panels is the later one is three times larger chances to contact with the developer and washing solutions. Therefore, if the developing solution (KOH) and the cleaning solution (H_2O) are mobile ion sources, it is presumed that the SOI value and luminance curve according to time between both panels will show different feature. In figure 7, the pixel images of (a) development 1 time and (b) development 3 times are compared, where it clearly represents that the panel with less development process shows better image, indicating that the mobile ions from the developing and cleaning solution would be main sources.

3.2.3. TOF-SIMS analysis

In the above experiment it was presumed that mobile ion appeared with developing solution (KOH) or cleaning solution (H2O). However, to know exactly where it was stacked, time of flight secondary ion mass spectrometry (TOF-SIMS) was carried out. Figure 8(a) is the cross section view image of the sample. The samples were analyzed by sputtering in the depth direction from the surface of the polyimide (PI) alignment layer. In figures 8(b) and (c), it is observed that the OH^- anion and the K^+ cation intensity is larger near the SiNx layer. Therefore, itis concluded that, during the development processes, all the ions from the developer on the surface of the color filter are not washed away completely and KOH ions are the cause of mobile ions.

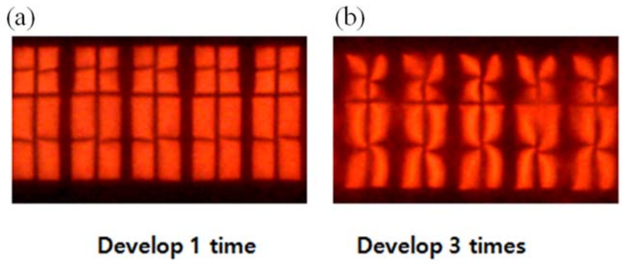

Figure 7. Microscope photograph after UV irradiation process of panel made by progressing one time development process and panel made by 3 times development process.

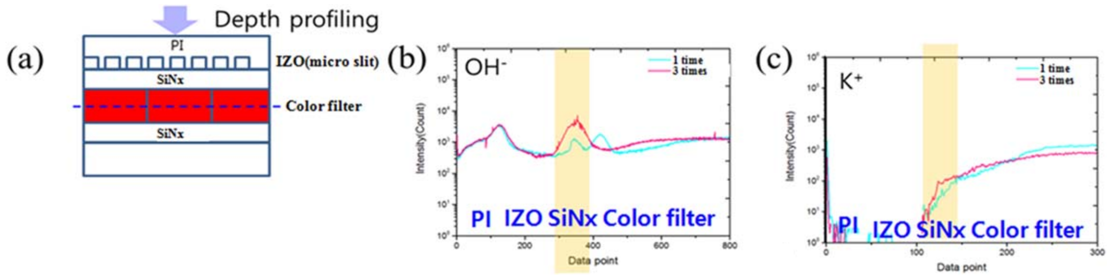

Figure 8. (a) Schematic representation of cross section view image of TOF-SIMS sample. (b) OH^- data analyzed by TOF-SIMS of the sample that was subjected to the development process once and three times. (c) K^+ data analyzed by TOF-SIMS of the sample that was subjected to the development process once and three times.

3.3. Mobile ion effect simulations

Techwiz 3D simulator was used to investigate whether the electric field by the DC voltage applied to the liquid crystal was distorted when mobile ions exit. The simulation parameters are shown in table 2. The voltage of top electrode is Vcom and the voltage of pixel electrode is Vp. When Vcom is 5 V and Vp is 0 V, the vertically aligned liquid crystals rotated in the micro-slit direction by the fringe field created by the micro-slit shaped pixel electrode. We simulated liquid crystal behavior for the four cases in figure 9. In reference condition, there is no charge at the interface between color filter and SiNx. As increasing the amount of charge, the simulation results of pixel image, LC director, and electric field are plotted to case 1 to case 3. As the amount of charge increases, the effect on the fringe field on the upper and lower plates is more affected. The results of case 2 are the most similar to the pixel images of the abnormal panel seen in figure 3. Therefore, it is concluded that the mobile charge density of about 2.0×10^{-10} C μm^{-2} weakened the fringe field applied between the upper and lower plate electrodes, resulting in abnormal behavior of the liquid crystal.

The upper electrode 5 V and the lower pixel electrode 0 V were applied. In the LC director, the brown arrow indicates the direction in which the liquid crystal molecules fall. In an electric field, a black arrow indicates an electrical line, and the thickness indicates the strength of the electrical line.

3.4. Minimization of mobile ion effects

To minimize the effect of KOH mobile ions, we increased the thickness of SiNx from 500 Å (reference) to 2500 Å. As the thickness of SiNx increases, the electric field induced by mobile ions will be decreased. Figure 10 shows pixel microscope images with respect to the SiNx thickness. For above SiNx thickness of 2000 Å, the distortion of pixel image is quite suppressed. The luminance reduction rate was also improved from 20% to less than 1%.

The thicker the SiNx, the thinner the thickness of the black brush lines of the liquid crystal. This indicates that the extent to which the liquid crystal molecules are aligned in the micro slit direction has increased.

4. Conclusions

In summary, we analyzed the behavior of abnormal liquid crystal molecules occurring during the UV irradiation process in PS-VA mode. Especially, the reason why the liquid crystal molecules rotate out of the micro-slit direction during the UV light irradiation while applying the voltage is the mobile ion derived from the developer

Table 2. Simulation parameters set of electric field near electrode (Techwiz 3D).

	Voltage		Pixel structure		Liquid crystal		SiNx	Charge amount
	Vcom [V]	Vp [V]	Line Width [μm]	Space Width [μm]	Dielectric constant [$\Delta\varepsilon$]	Refractive Index [Δn]	Dielectric constant [ε]	[C/um^2]
value	5	0	3	3	−3.6	0.1	6.6	Variable

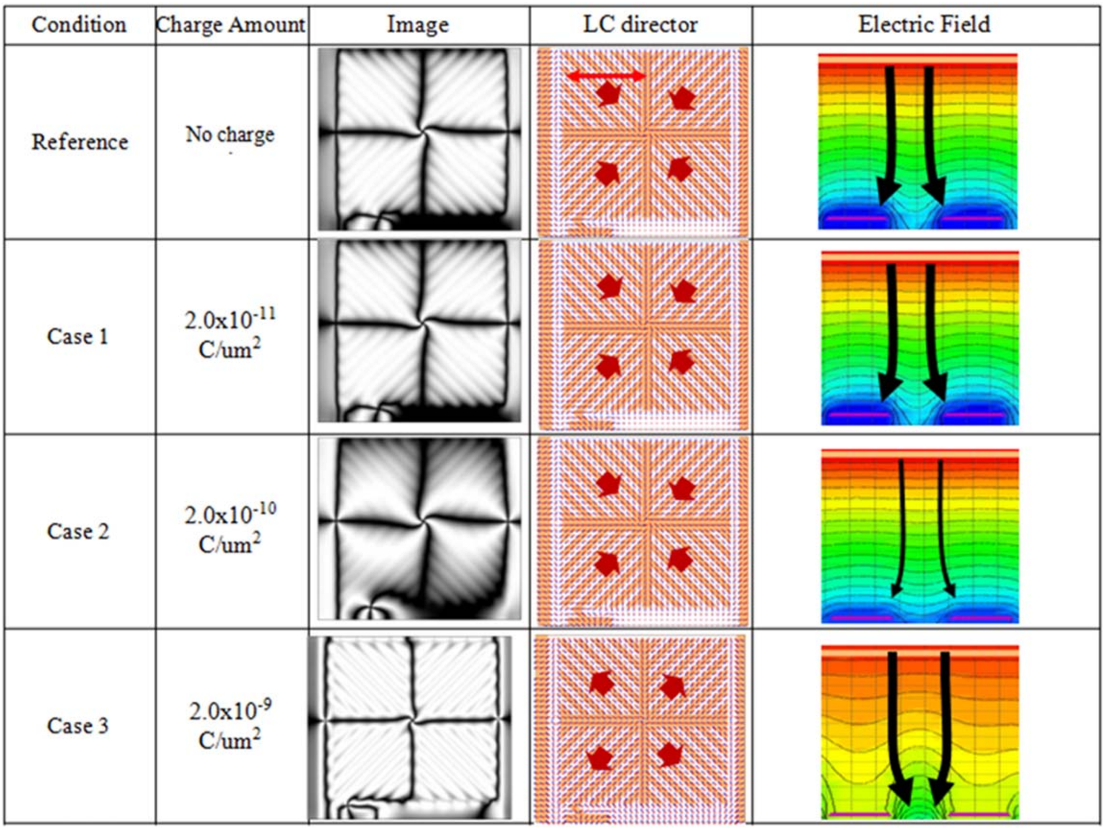

Figure 9. Results of electric field simulation according to the amount of mobile ion using Techwiz 3D.

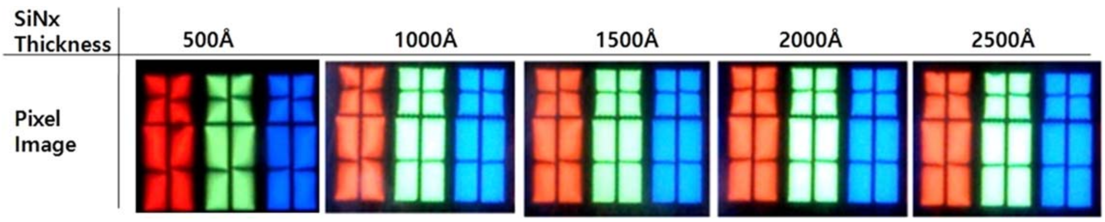

Figure 10. Microscope images of pixel made with UV irradiation process while changing SiNx thickness.

of the color filter by using EFM, TOF-SIMS methods. The behavior of these abnormal liquid crystals can occur when the amount of mobile ion charge is about 2.0×10^{-10} C μm^{-2}. To reduce the mobile ion induced electric field effect, it was found that the thickness of the SiNx layer above the color filter should be increased to over 2000 Å.

Acknowlegment

This work was supported by the Future Growth Engine Program (10079974, Development of core technologies on materials, devices, and processes for TFT backplane and light emitting front plane with enhanced stretchability above 20%, with application to stretchable display) funded By the Ministry of Trade, Industry & Energy(MOTIE, Korea).

ORCID iDs

Nakcho Choi https://orcid.org/0000-0001-7176-9595

References

[1] Kimura N *et al* 2005 *Sid 2005Digest* **36** 1734
[2] Kim S *et al* 2004 *Journal of the Society for Information Display* **12** 353
[3] Hanaoka K *et al* 2012 *Sid 2012Digest* **41** 1200
[4] Kim S G *et al* 2007 *Applied Physics Letters* **90** 261910
[5] Kim S M *et al* 2009 *Japanese Journal of Applied Physics* **48** 032405
[6] Kim S G *et al* 2008 *Journal of Physics D: Applied Physics* **41** 055401
[7] Suwa S *et al* 2010 *Sid 2010Digest* **41** 595
[8] Min Young J I N *et al* 2007 *Japanese Journal of Applied Physics* **46** 1585
[9] Yoon W-J *et al* 2017 *ACS Omega* **2** 5942
[10] Lee Y-J *et al* 2009 *Optics Express* **17** 10298
[11] Lyu J J *et al* 2011 *Journal of Physics D: Applied Physics* **44** 325104
[12] Kwon Y R *et al* 2016 *Journal of Physics D: Applied Physics* **49** 165501
[13] Lee Y-J *et al* 2010 *Japanese Journal of Applied Physics* **49** 030209
[14] Yeh P and Gu C 2006 *Optics of Liquid Crystal Displays* (New York: Wiley)
[15] Choi N *et al* 2015 *IMID 2015* P1, 87
[16] Girard P 2001 *Nanotechnology* **12** 485