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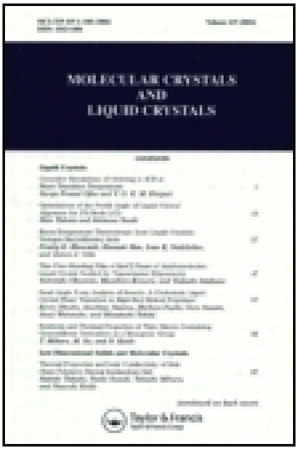

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Photo-Induced Structural Change of and Interaction Between Organic Materials in Liquid Crystal Display Panel

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Structural changes of and the interactions between organic materials in liquid crystal display panel after UV exposure were systematically investigated using FT-IR, XPS, AFM, and LC-ESI-MS. When the photo-curing of the sealant was imperfect during the assembly of LCD panel, both the components in the sealant such as UV-initiator contaminated the LC's and the stray UV light oxidized the benzene rings and other chemical bonds in the polymer backbone of the alignment layer. This resulting contamination of LC's and degradation of the alignment layer could disturb the pretilt angle of the VA-mode LC's and cause the display defects on the LCD panel. In this regard, careful control of the photo-curing of the sealant will be required for precise alignment of the LCD panel and better performance of the display.

Keywords: LCD panel; liquid crystal; photo-initiator; sealant; UV curing

I. INTRODUCTION

Market for flat panel display has been developed tremendously and the revenue from all kinds and sizes of flat panel display (FPD) grew to exceed $100 billions in 2007 [1]. The higher-than-expected market expansion of FPD has been accomplished recently and this trend will continue due to the variety of applications of FPD. Amongst the flat

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display displays, TFT liquid crystal display (TFT-LCD) has been leading FPD technology due to the increasing panel size, the higher image quality, the light weight, and the rapid declining of the panel cost.

The manufacturing processes of LCD panel are very sophisticated and complicated. One of a key process of LCD panel is photolithography composed of four basic steps; 1) photo resist coating, 2) UV exposure, 3) development, and 4) etching. As LCD panel is made up of conducting & semiconducting materials and also organic materials of the color filter, liquid crystal, the sealant, etc., photolithography, esp. UV exposure process, should be carried out carefully and monitored precisely to make the defect-free LCD panels.

It is well known that the UV exposure to the organic materials can lead the extensive changes in the chemical structures and physical properties. The chemical structural changes of polymer materials by UV light are frequently applied to make the structural modification with special applications, such as the photo alignment polymer, integrated optical circuits for telecommunication, and sensor applications, etc. [2–4]. In other cases, some studies showed that polymer materials irradiated by UV could result into the radical formation, followed by the bond breaking of the main chains and thus oxidation of polymer materials to the deterioration of physical properties [5].

However, there have been few studies concerning the structural changes of and interactions between organic materials in the LCD panel, caused by UV light irradiation.

In this paper, we studied the photo-induced structural changes of and interactions between organic materials in LCD panel during UV-curing of the sealant, in which the alignment layer, liquid crystal, and the sealant are altogether involved in this step. Therefore, our investigation has been performed using the test cell in terms of various experimental conditions to understand the various artifacts phenomena occurred during the assembly of LCD panel.

II. EXPERIMENTAL

All test samples were prepared and investigated by the-state-of-the-art analytical techniques in our laboratory. Figure 1 shows a schematic illustration of a test cell and UV exposures on the seal line focused in this study. When curing sealant by UV exposure, we intentionally applied UV light to cure either sealant fully or sealant partially with surrounded area. In order to describe these experimental procedures depicted in Figure 1, new terminologies of full-photo and partial-photo have been adopted in this paper. ‘Full-photo’ has been used when the UV light directed to only sealant, leading it to

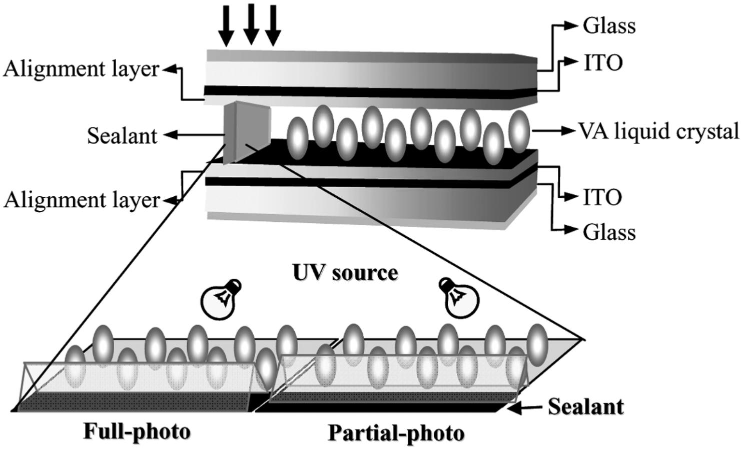

FIGURE 1 Schematic illustration of test cell and UV exposures on the seal line area of LCD panel.

be fully cured. On the other hand, ‘Partial-photo’ has been employed to describe the situation where the sealant and the surrounding area are exposed to the UV light together and the sealant is not fully cured. LC and the alignment layer could be UV-damaged during this procedure.

Test sample used in the study was fabricated as follows. A polyimide (Japan Synthetic Rubber Co.) of the alignment layer was dissolved in N-methylpyrrolidone and spin coated onto two $5 \times 5\,\text{cm}^2$ indium-tin-oxide (ITO) glass with a film thickness of less than 100 nm. Two glasses coated with polyimide were heated at 85°C for 30 minutes, followed by baking at 220°C for 10 min. After that, a UV-curable acrylate polymer (Sekisui Co. Japan) of a sealant was drawn at the edge of the glass with the width of 1 mm. Subsequently, LC of a vertical alignment (VA) mode was dropped onto the surface of the alignment layer. LC is a mixture of 10 single compounds with the negative dielectric anisotropy and obtained from Merck Advanced Technologies (MAT). Finally this pair of glasses was assembled by UV light irradiation to the sealant with 325 nm wavelength and $300\,\text{mJ/cm}^2$ sensitivity.

For investigating the structural changes of the sealant, the alignment layer, and liquid crystal during ‘Full-photo’ and ‘Partial-photo’ processes, the test cell was decaped, followed by removing the liquid crystal with Isopropanol (IPA) and attached to the specimen stage for analysis. X-ray photoelectron spectroscopy (XPS) and the Fourier transform infrared (FT-IR) spectroscopy were carried out for elucidating the

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structural changes and interactions among the organic materials. XPS was performed using an Ulvac-Phi Quantera system with the monochromatic X-ray source of Al with the pass energy of 70 eV at the power of 300 mW (the beam size of X-ray source, 60 μm the pass energy for high-resolution spectra, 17.90 eV (0.05 eV steps); a take-off angle, 75° relative to the surface plane). All the XPS spectra were corrected for charging effect by referencing the C 1s peak of hydrocarbons to 285.0 eV. High resolution spectra were analyzed to identify various chemical species present. Each spectrum was curve-deconvoluted using the XPSPEAK2 software [6,7]. Quantification of XPS spectra was achieved by curve integration after baseline correction using a Shirley baseline equation and correcting the integrated area using each elemental sensitivity factor. The ATR (Attenuated Total Reflection)-FT-IR spectra were collected using a Bruker IFS66S spectrometer with the germanium crystal at the angle of 65°(scan time: 64, resolution: 4 cm^{-1}). For finding contaminants in LC near the sealant and elucidating the structural changes of them, if any, the positive ion electrospray mass spectra (LC-ESI-MS) and collision-induced-dissociation (CID) spectra (MS/MS mode) were recorded with a ThermoFinnigan LTQ spectrometer (electrospray voltage, 3.2 kV; capillary temperature, 200°C; sheath gas, N_2). The MS controlled the total ion chromatograms and mass spectra were recorded using the ThermoFinnigan Xcalibur software (San Jose, CA). Helium was used to improve trapping efficiency as the collision gas for the CID experiments. The LC extract was dissolved in acetonitrile and methanol mixture to 1000 times dilution (0.1 total volume %) and a 20 μl aliquot of the solution was injected onto the LC-ESI-MS system. The surface morphology of test cells was obtained by atomic force microscopy (AFM) (Seiko Instruments Co., SPA 500HV) at 293 K in air.

III. RESULTS AND DISCUSSION

1. The Sealant

In Table 1 are shown the components of the sealant used in this study. The UV-curable sealant is made up of an oligomer, a monomer mixture, photo-initiators, and additives, different from the thermal curing system using the solvent.

The chemical and structural changes of the sealants in ‘Full-photo’ (below ‘Full-photo’ sealant) and ‘Partial-photo’ test cells (below ‘Partial-photo sealant’) were investigated using the Fourier transform infrared (FT-IR) spectroscopy. In Figure 2, the 1600 cm^{-1} and 690 cm^{-1} of ‘Full-photo’ sealant can be assigned to an unsaturated/aromatic

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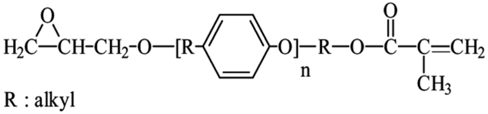
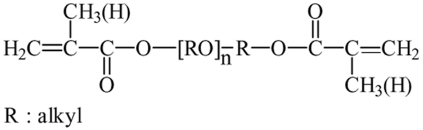
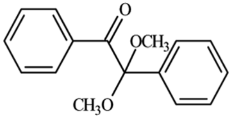
TABLE 1 The Components of the UV-Photo Curing Sealant Used in This Study

Component	Content (%)		Chemical structure
Oligomer	30	Phenyl epoxy acrylate	
Monomers	25 20	Difunctional methacrylate Difunctional acrylate	
Photo-initiator	1	Benzil-dimethyl ketal	
Additives	20 4	Silica & Tetramethyloxysilane Etc.	

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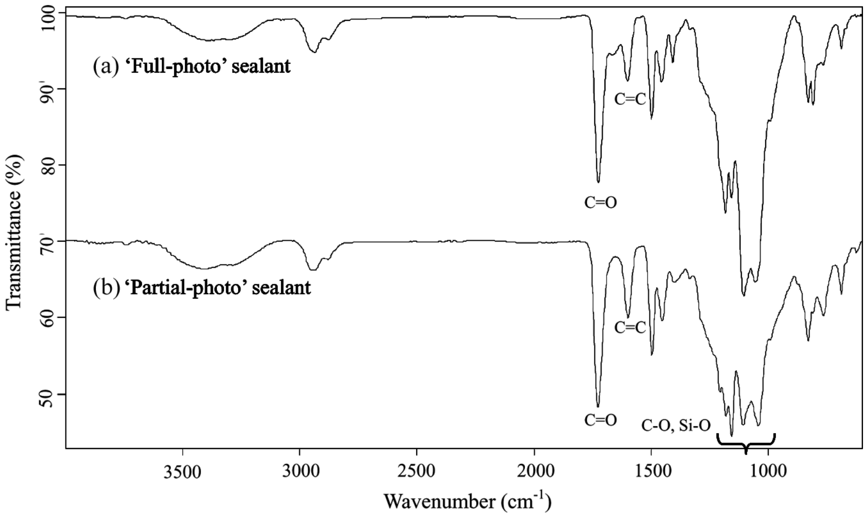

FIGURE 2 FT-IR spectra of 'Full-photo' sealant (a) and 'Partial-photo' sealant (b).

C=C stretching and an unsaturated/aromatic C=C-H out-of-plane, respectively. The intensities of these peaks decreased, in comparison with those of the 'Partial-photo' sealant. On the other hand, the peaks of the 1120 cm^{-1} and at 1030 cm^{-1} of 'Full-photo' sealant, an ether C-O-C stretching and a silica Si-O stretching, showed the increase in intensity compared with those of the 'Partial-photo' sealant in Table 2. [8].

TABLE 2 Characteristic peaks and assignment of the UV-curing sealant used in this study [8]

Characteristic peaks (cm^{-1})	Assignments
3500~3100	-OH str.
3000~2800	C-H str.
1725	Acryl $\underline{O}=\underline{C\text{-}O}$ str.
1600	Unsaturated/aromatic C = C str.
1497	Aromatic ring str.
1450	Aromatic ring str./CH_2 bend
1280~1150	Epoxy C-O-C str. & Acryl $O=\underline{C\text{-}O}$ str.
1120	Ether C-O-C str.
1030	Silica Si-O str.
850~800	C-C skeletal/C-O sym. str.
760	Epoxy C-O-C def.
690	Unsaturated/aromatic $C=\underline{C\text{-}H}$ oop

The above-mentioned phenomena can be explained that there are un-reacted curing site, C=C & epoxy C-O-C bonds, and less C-O & Si-O bonds in the 'Partial-photo' sealant, due to the un-reacted photo-initiator and additives. These materials were found to be the cause of the deterioration of the display by the XPS and Mass spectrometry measurements in the followings.

2. LCs

The chemical and structural changes of the liquid crystal surrounding the sealant were studied with FT-IR in Figure 3. The FT-IR spectra of LCs of 'Full-photo' cell (below 'Full-photo' LC) (a) and of 'Partial-photo' cell (below 'Partial-photo' LC) (b) show no difference, compared with the raw LC spectrum.

Although the structural features of liquid crystalline materials for TFT-LCD's mostly have rigid cyclic core ring systems that are composed of 2 or more cyclohexyl and/or phenyl rings substituted with halogen atoms and nonpolar alkyl or alkenyl groups [9], LC molecules are electrically neutral and have moderately nonpolar properties. As LC-ESI-MS and MS/MS mode could detect the polar species with the wide range of 100~100,000 molecular weight, it is very useful to analyze the high molecular weight and polar contaminant in liquid crystal from the sealant and the alignment layer, if any. It is kept in mind that as LC-ESI-MS method is impossible to detect the non-polar

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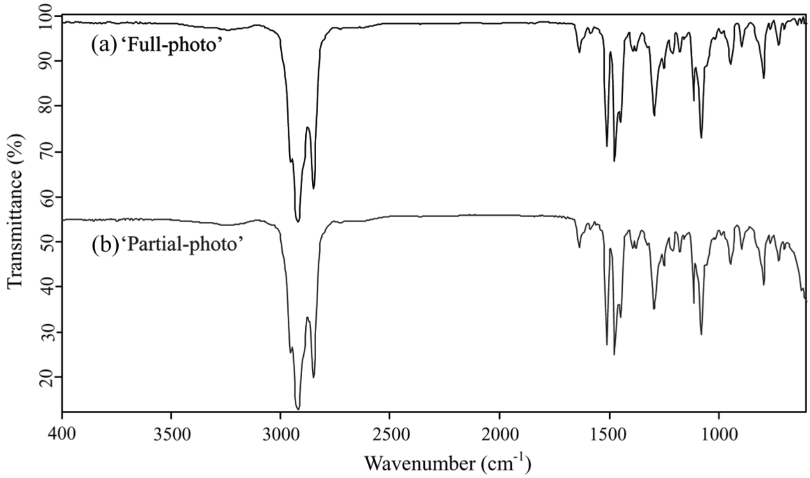

FIGURE 3 FT-IR spectra of 'Full-photo' LC (a) and 'Partial-photo' LC (b).

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species, non-polar single liquid components used in this study couldn't be detected in LC-ESI-MS. Figure 4 shows the LC-ESI-MS spectra of 'Full-photo' LC (a), 'Partial-photo' LC (b), and the sealant (c). In Figure 4, only column contaminants were detected in 'Full-photo' LC (Fig. 4(a)), but new m/z peaks at 279.18, 389.18, and 409.18 were appeared in 'Partial-photo' LC (Fig. 4(b)). These new m/z peaks were very similar to MS spectra of the sealant, identified as UV-initiator (256(MW) + 13(Na^+ adduct)) at 279.18 m/z, an oligomer or a monomer at 389.18 and 409.18 m/z. For the accurate identification of these new m/z peaks, MS/MS profiles at m/z 279.18 of 'Partial-photo' LC and the sealant with the collision energy 30 kV were observed in Figure 5.

Figure 5 shows that the MS/MS profiles at m/z 279.18 of 'Partial-photo' LC and the sealant's UV-initiator show perfectly same pattern. This means that 'Partial-photo' LC was contaminated with the uncured UV-initiator remained in 'Partial-photo' sealant. This phenomenon could be understood as the UV-initiator has a benzene ring and a polar component, very similar structure to LC, enough to mix UV-initiator and LC. The existence of the contaminant in LC itself could be responsible to disturb the alignment of VA-mode LC in LCD panel.

3. The Alignment Layer

The alignment layer for VA-mode consists of a polyimide type polymer, a thermo-curing epoxy initiator, and solvent mixture(NMP (N-methyl-2-pyrrolidone)/GBL(γ-butyrolactone)/BC(butyl cellusolve) = 4/3/3) (solid content: 3 wt%). The polyimide type polymer, 1,2,4-tricarboxy-3-carboxy-methylcyclopentane (TCAAH) and phenylene diamine (PDA), is shown in Figure 6.

The structural changes at the surface of the alignment layer were analyzed using XPS, which gives the information of the chemical bonding state and the quantity of the atoms. After acquiring XPS spectra of the alignment layer of 'Full-photo' cell (below 'Full-photo' alignment layer) and of 'Partial-photo' cell (below 'Partial-photo' alignment layer), we carried out curve fitting of those spectra using a Shirley baseline equation and correcting the integrated area using each elemental sensitivity factor as shown in Figure 7. The result of chemical bond composition of the quantitative of atoms from the curve fitted C1s XPS spectra were summarized in Table 3 [10–11]. Compared Figure 7(a) with Figure 7(b), it is observed that intensities due to the peaks of C=C, C-C and O=C-N-C=O decrease and on the other hand, the intensities attributed to -HN-C=O and –COOH increase. This means that there is the dissociation of imide bond of

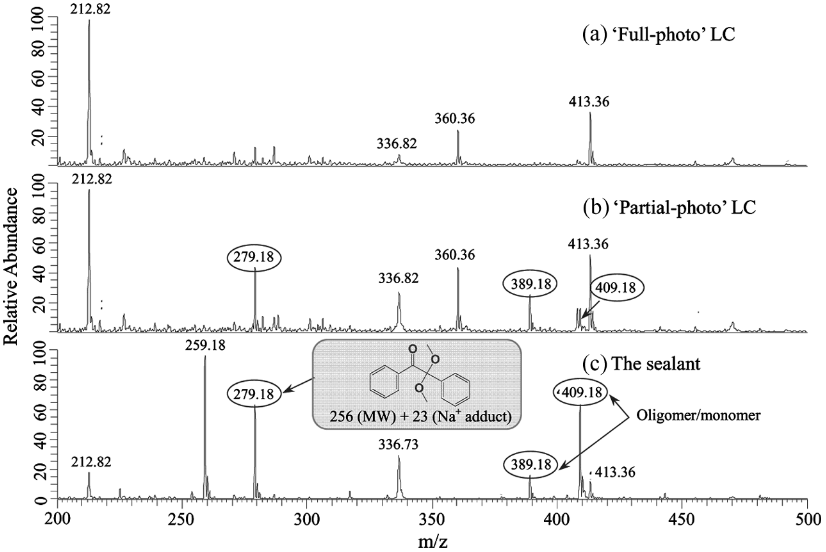

FIGURE 4 LC-ESI-MS mass spectra of 'Full-photo' LC (a), 'Partial-photo' LC (b) and the sealant (c).

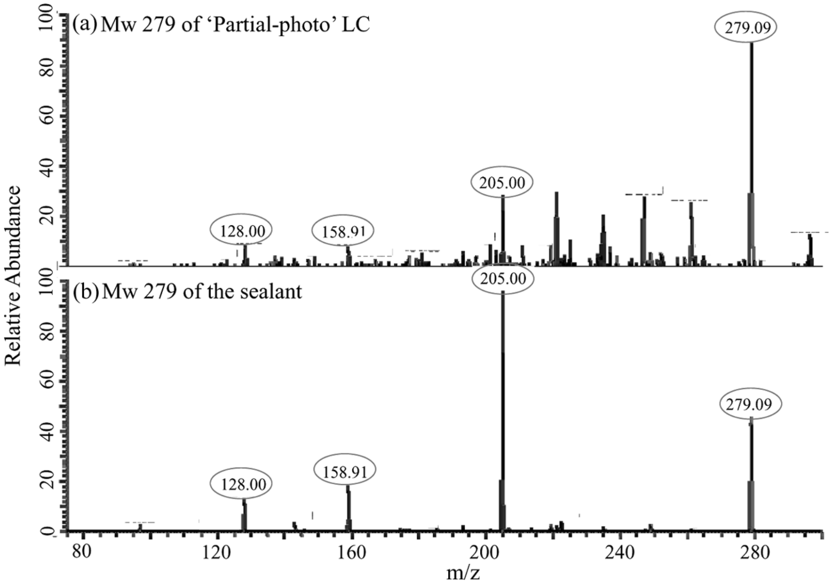

FIGURE 5 MS/MS spectra of the molecular ion at Mw 279 of 'Partial-photo' LC (a) and the sealant (b).

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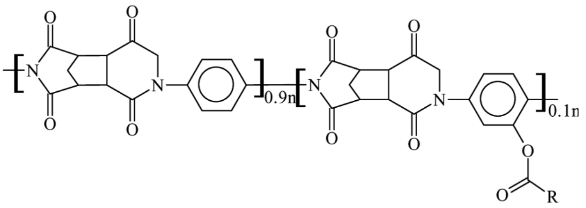
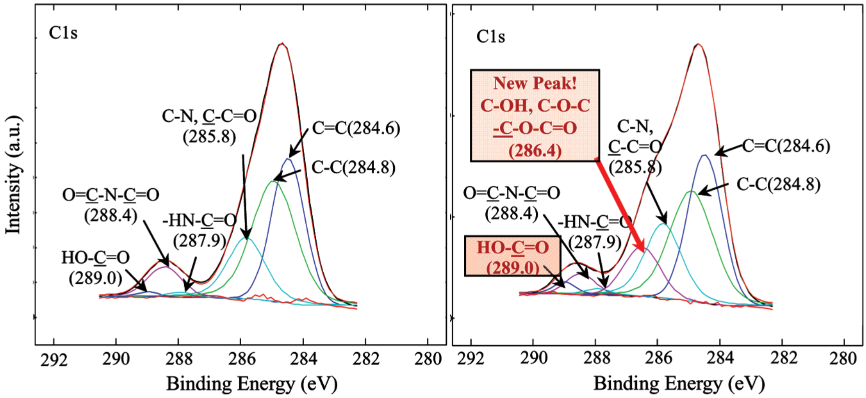


FIGURE 6 The repeating units of the polyimide film for PVA mode used in this study.

the alignment layer into amide and carboxylic acid groups in 'Partial-photo' cell. Also, Figure 7(b) shows new carbon component peak occurred at 286.4 eV, identified as various ether bonds, C-OH, C-O-C, -C-O-C=O, which indicates that 'Partial UV irradiation' at the alignment layer during the sealant curing induced C-OH, C-O-C, and -C-O-C=O linkage in polyimide backbone, from the C=C and C-C bond breakage/oxidation.

The surface topographies of 'Full-photo' and 'Partial-photo' alignment layer were observed with atomic force microscope (AFM) in Figure 8.

Figure 8(a) and (b) show the 3D AFM images of 'Full-photo' and 'Partial-photo' alignment layer surfaces, and Figure 8(c) is the RMS



(a) 'Full-photo' alignment layer

(b) 'Partial-photo' alignment layer

FIGURE 7 Curve-fitted C1s XPS spectra and chemical bond composition of 'Full-photo' alignment layer (a) and 'Partial-photo' alignment layer (b).

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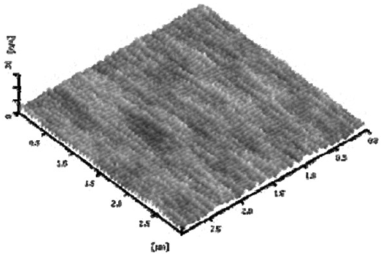
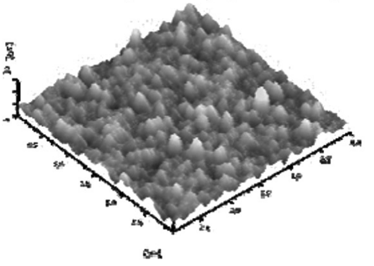
TABLE 3 Chemical bond composition of curve-fitted C1s XPS spectra of 'Full-photo' alignment layer and 'Partial-photo' alignment layer [10,11]

Chemical bond composition	'Full-photo'	'Partial-photo'
C=C	33.06	31.18
C-C	39.75	33.06
C-N, C-C=O	18.14	18.02
C-OH, C-O-C, -C-O-C=O	–	10.86
-HN-C=O	0.96	1.17
O=C-N-C=O	7.35	3.82
-COOH	0.74	1.89

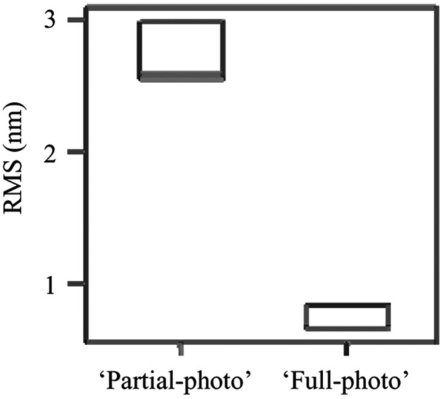
plot of surface roughness derived from Figure 8(a) and (b). Surface roughness of 'Partial-photo' alignment layer is definitely higher than that of 'Full-photo' alignment layer. This result can be explained due to the surface oxidation, which is in a good agreement with that of XPS result. As the surface roughness of the alignment layer of the test cell increase, the pretilt angle (90°) of VA-mode LC on the alignment layer could be disturbed and lead to the display artifacts, such as the light-leak, the image sticking, etc.



(a) 'Full-photo' alignment layer



(b) 'Partial-photo' alignment layer



(c) Surface Roughness

FIGURE 8 AFM images of 'Full-photo' alignment layer (a) and 'Partial-photo' alignment layer (b) and their RMS plot (c).

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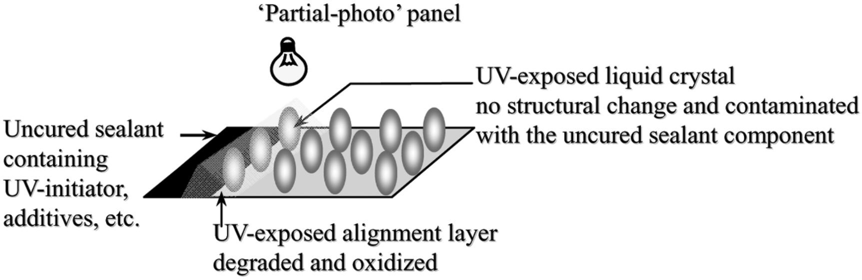

FIGURE 9 Scheme of the structural change of and interaction between organic materials in LCD panel used.

IV. CONCLUSIONS

The structural changes of and interactions between organic materials in the LCD panel caused by UV light irradiation has been studied with the test cell using a series of FT-IR, XPS, AFM, and LC-ESI-MS.

When UV exposed to both the sealant and the surrounding area accidentally due to the misalignment of the test cell, the sealant was cured imperfectly and the alignment layer was also UV- damaged. The photo-initiator unused in the sealant squeezed out into Liquid Crystal and the benzene ring and C-C linkage of the alignment layer degraded and oxidized to form the oxidized chemical groups, -COO- and –COOH, shown in Figure 9. The existence of the contaminant in LC and the degradation/oxidation of the alignment layer in LCD panel resulted in the change of the pretilt angle 90° of VA-mode LC, lead to the degradation of the image quality of the LCD panel.

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