Reduction of the Residual DC in the Photoaligned Twisted Nematic Liquid Crystal Display Using Polymerized Reactive Mesogen

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A residual direct current (DC) voltage property in the twisted nematic liquid crystal display (TN-LCD) using photoaligned polyimide is studied by the capacitance–voltage hysteresis method. A residual DC is greatly reduced in the photoaligned cell with an additional polymerized layer on a photoaligned layer with the help of a UV-curable reactive mesogen. The surface of the photoaligned layer becomes much more polar than that of the rubbed layer, possibly leading to a larger trapping of ions on the photoaligned layer than on the rubbed polyimide layer. The polar surface can be modified with an additional proposed polymer layer and, thus, the low residual DC voltage can be achieved.

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ecently, liquid crystal displays (LCDs) have been used for all display fields such as notebooks, monitors, mobile phones, and LCD televisions. For the industrial production of LCDs, a uniform alignment of liquid crystal (LC) molecules should be achieved through an anisotropically treated surface on substrates. The process should be easily achievable and a low-cost one with no defects at all. Some of the most widely used technologies for LCD fabrication involve homogeneously aligned LC modes such as twisted nematic (TN)¹⁻⁴ mode, in-plane switching (IPS)⁵ mode, and fringe-field switching $(FFS)^{6-9}$ mode. To achieve a homogenous alignment, a substrate requires an additional process that induces LC directors to a preferred direction. Various methods such as rubbing,¹⁰⁻¹³⁾ oblique deposition of inorganic oxides such as SiO₂,¹⁴⁾ use of Langmuir–Blodgett film,¹⁵⁾ and nonrubbing¹⁶⁾ for obtaining uniform alignment have been proposed. Among them, planar anchoring of the nematic director in the conventional LCD has been mainly achieved by rubbing a polymer film, polyimide (PI) that is, by generally creating microgrooves on the polymer surface and inducing surface anisotropy in molecular orientation on the surface of the polymer. However, the rubbing process inevitably has several demerits such as the generation of electrostatic charges and dust from friction between the rubbing cloth and polymer surface. Moreover, it is difficult to obtain a uniform alignment for the large-size display or multidomain LC alignment for a wide viewing angle.

To solve these problems, research studies on noncontact alignment treatment such as ultraviolet (UV) irradiation,^{17,18)} ion beam,^{19,20)} and plasma irradiation^{21,22)} have been reported. Among these noncontact processes, the photoalignment technique has the greatest potential to replace the conventional rubbing method. Recently, we have reported a novel photoalignment material based on soluble aromatic polyimide with chloromethyl side groups, which exhibits excellent photosensitivity and superior thermal stability.^{23–25)} However, the noncontact processes also have some disadvantages such as weak anchoring energy and high residual direct current (DC) voltage. In order to generate LC alignment using photodecomposable PI films, a shortwavelength UV irradiation is needed. When the photodecomposable PI film is exposed to UV irradiation, the backbones of the PI chains lying in the same direction with the linearly polarized UV are decomposed and as a result the surface of the photo-alignment layer gains polarity.²⁶⁾ The trapped ions on the surface with high polarity later create several problems by lowering the resistivity of the LC material and thus degrade the image quality and reliability of the device. Image sticking and flickering problems also arise in the product due to the increase of the number of trapped ions in interfaces between LC and alignment layers. To achieve more reliability from a photoalignment technique, therefore, the above-mentioned problems should be rectified.

In this paper, we have studied the reduction of a residual DC in a photo-aligned twisted nematic liquid crystal display (TN-LCD) by using a UV-curable reactive mesogen $(RM)^{27-29}$ to improve the image sticking phenomenon. This phenomenon has been discussed by comparing the surface energy of the newly developed film with those obtained by conventional rubbing methods.

For the experiment, we fabricated photo-aligned, photoaligned with RM, and rubbed TN cells with cell gaps of 4.7, 4, and 4.6 µm, respectively. As an alignment material, we synthesized a soluble aromatic polyimide containing chloromethyl side groups, which can align liquid crystals either by rubbing or by photoalignment, according to our previous paper.^{23,24)} The photoaligned layers were exposed to polarized UV light (254 nm, 1.3 mW/cm², 60 min) using UV exposure system with 42% of an extinction ratio (Nanotek NT-HGIK-V09-SOR) prior to the fabrication of TN cells. We used an LC material (from Merck) with a positive dielectric anisotropy ($\Delta \varepsilon = +7.4$ at 1 kHz) and with elastic constants $K_{11} = 11.7$ pN, $K_{22} = 5.1$ pN, and $K_{33} = 16.1$ pN at 20 °C.

For the TN cells photo-aligned with RM, an LC/RM mixture that was prepared by mixing the LC with RM (Merck RM 257) containing 1 wt % photoinitiator (Merck Irgacure 651) in the weight ratio of 99.6 : 0.4 was used. Initially, the RM molecules are twisted homogeneously following the local LC orientation due to the use of crossly placed photoaligned homogeneous alignment layers on each substrate. Next, the concentration of the RM molecule becomes higher in the vicinity of the alignment surface and relatively lower in the middle layer as reported in our previous paper.³⁰⁾ When the concentration of the RM molecule is very small compared with the concentration of LC, a phase separation between RM molecules and LC occurs before UV exposure.

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Fig. 1. POM images in the bright and dark states of photoaligned (a, d), RM-coated photoaligned (b, e), and rubbed (c, f) TN cells, respectively.

Under this condition, the cell is exposed to UV light $(365 \text{ nm}, 1.5 \text{ mW/cm}^2, 17 \text{ min})$ and thus, the RM molecules are polymerized at the surfaces. Consequently, the LCs in the bulk relax to the crossly placed original homogeneous state while the surfaces have crossed orientation along the director with an additional polymer layer.

The textures of the three different cells were studied under a polarizing optical microscope (POM; Nikon DXM1200) with and without applied voltage. To confirm the residual DC voltages, the voltage-dependent capacitance was measured using an LCR meter 4284A (Agilent Technologies). Finally, surface energies of the three substrates with different surface ingredients were estimated by measuring the contact angles by using distilled water (H₂O) and diiodomethane (CH₂I₂) droplets.

After fabrications, in order to confirm if the cell is switching properly, the dark and white states were observed using a POM in transmittance mode. Figure 1 shows POM images in the dark and white states of the photo-aligned, photo-aligned with RM, and rubbed TN cells. In the off states of each case, only the different transmittance colors with high brightness were observed because of differences in the cell gaps, as shown in Fig. 1. In addition, no defects related to the RM monomer are observed [see Fig. 1(b)]. As a result, it was confirmed that uniform transmittances were generated in all the cases, as shown in Figs. 1(a)-1(c). In the on states of each case, uniform dark states without a desclination line were observed in all the cases. This indicates that the vertical electric field tilts up the LC molecules to the field direction in the whole region, as shown in Figs. 1(d)-1(f). Thus, for the newly designed cell, having a photoaligned layer with RM did not create any defect due to the addition of RM on the photoaligned surface, which was also confirmed from the dark state of the corresponding cell.

To estimate the residual DC voltages, the voltagedependent capacitance was measured using an LCR meter. In these measurements, DC voltage was applied to the cell by increasing and decreasing the voltage from -10 to +10 V with a step bias voltage of 0.1 V/s. Hysteresis levels *a* and *b* defined as the difference in voltages between increasing and decreasing show 50% of maximal capacitance (see Fig. 2). The residual DC voltage is defined as

Residual DC =
$$\frac{a+b}{2}$$



Fig. 2. Voltage-dependent capacitance hysteresis in the (a) photoaligned, (b) RM-coated photoaligned, and (c) rubbed TN cells.

Figure 2 shows the residual DC voltage characteristics of the TN cells with different surface treatments on alignment layers. The residual DC voltages are 0.60, 0.20, and 0.35 V in Figs. 2(a), 2(b), and 2(c), respectively. It is shown that the TN cell of the RM-coated photoaligned layer exhibits the smallest hysteresis of LC capacitance as shown in Fig. 2(b). From this result, we can confirm that the polymerized RM layer is somehow screening the trapped ions in the photoalignment material.

To find out why the residual DC of the photoaligned TN cell is larger than those of the others, we calculated the surface energy of each alignment layer. The contact angles of three substrates with different surface states were measured by using diiodomethane (CH_2I_2) and distilled water (H₂O). The polar, dispersion, and total surface energy were calculated from the result of contact angle measurements by using the Owens–Wendt–Geometric mean equation,³¹⁾ which is suitable for obtaining the surface energy of most of the polymer. The Owens–Wendt–Geometric mean equation is given as

Table I. Surface energy components of the photoaligned layer, RM-coated photoaligned layer, and rubbed layer (unit: mN/m).

	Photoaligned layer	RM-coated photoaligned layer	Rubbed layer
Dispersion energy	37.54	43.80	41.08
Polar energy	12.70	3.26	4.30
Total surface energy	50.24	47.06	45.38

$$\begin{split} \gamma_1(1 + \cos \theta_1) &= 2 \bigg(\sqrt{\gamma_1^d \gamma_s^d} + \sqrt{\gamma_1^p \gamma_s^p} \bigg), \\ \gamma_2(1 + \cos \theta_2) &= 2 \bigg(\sqrt{\gamma_2^d \gamma_s^d} + \sqrt{\gamma_2^p \gamma_s^p} \bigg), \end{split}$$

where γ_s is the surface energy of the alignment layer, γ_1 , γ_2 , θ_1 , and θ_2 are the surface energies and contact angles of distilled water and diiodomethane, respectively. Superscripts *d* and *p* are dispersion energy and polar energy, respectively.

The measured θ_1 (H₂O) and θ_2 (CH₂I₂) of the photoalignment layer, RM-coated photo-alignment layer, and rubbed alignment layer are 60 and 44°, 77 and 31°, and 76 and 37°, respectively. Surface energies of distilled water and diiodomethane are obtained from the literature.³²⁾ Table I shows the calculated surface energy components of three samples. The total surface energy was slightly decreased in the order of photoaligned layer > RM-coated photoaligned layer > rubbed layer. While the dispersion energies of all three samples were similar to each other, the polar energy term shows a significant difference. The polar energy of the photoaligned layer is estimated to be 12.70 mN/m, which is the highest among the three samples due to the generation of polar groups such as amine acid and carboxylic acid on the surface during the UV irradiation.²⁴⁾ As a result, residual DC of the photoaligned TN cell has been increased, because ions are piled on the surface of the polar photoaligned layer. On the other hand, the RM-coated photo-aligned sample exhibits significantly reduced polar energy (3.26 mN/m), which is even smaller than that of the rubbed layer. The above result also suggests that the polymerized RM layer covering the photo-aligned polyimide layer effectively reduces the exposure of surface polar groups to the TN cell while retaining the homogeneous orientation of LC.

To confirm the reliability of cells, we measured residual DC voltage as a function of time, as shown in Fig. 3. It is shown that the residual DC voltage of the RM-coated TN cell with the photoaligned polyimide has almost no change even after 7 days comparable to that the of TN cell with a rubbed layer. On the other hand, the same parameter increases by a large amount in the case of the TN cell with pure photoalignment for the same period of time. The reason is that the ions are more accumulated on the surface of the pure photoaligned layer with high polarity, especially under applied voltage during the residual DC voltage measurement.

To summarize, we have investigated the image-sticking property in the TN cell with a photo-aligned polyimide alignment layer by measuring the residual DC voltage and polar surface energy. To overcome the image-sticking problem caused by ion trapping on the photo-aligned polyimide surface, we suggest a novel method of *in situ* photopolymer-



Fig. 3. Residual DC voltage as a function of time in the photoaligned, RM-coated photoaligned, and rubbed TN cells.

ization of RM on the surface of the alignment layer, which screens the polar surface of the photo-irradiated polyimide while retaining the homogeneous orientation of LC. It is found that the residual DC voltage and polar surface energy are simultaneously reduced close to that of the rubbed layer. This indicates that the polymerized RM layer on the surface of the substrate helps to reduce the residual DC voltage and may improve image sticking properties in the photoaligned TN cell. This can be an important step to improvise the photoalignment technique without any ions generated.

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