Polymer-stabilized pretilt angle on the surface of nanoparticle-induced vertical-alignment surface for multi-domain vertical-alignment liquid-crystal display

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Abstract — By introducing polyhedral oligomeric silsesquioxane (POSS) nanoparticles along with a controlled amount of UV-curable reactive mesogen (RM) into a liquid-crystalline (LC) medium, a multi-domain vertical-alignment LC device was successfully demonstrated. The device, possessing a vertically aligned LC director in four different azimuthal directions, exhibited a fast response time and wide-viewing-angle characteristics, in the absence of conventional polymer-type vertical-alignment layers. Electro-optic characteristics of the fabricated device, before and after UV curing of the cell, were studied. The surface morphology of the substrate surfaces were analyzed by using field-emission scanning electron microscopy (FESEM). The experimental results show that the technology will possibly be applicable to cost-effective vertical-alignment liquid-crystal devices and is suitable for green-technology liquid-crystal displays.

Keywords — *Liquid crystal, nanoparticles, vertical alignment, polymer stabilization.*
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1 Introduction

In recent years, due to their expanding requirement in the display market, wide-viewing-angle liquid-crystal displays (LCDs) have attracted considerable attention of researchers and technologists. Various driving modes, such as in-plain switching (IPS),[1,2] fringe-field switching (FFS),[3–7] patterned vertical alignment (PVA),[8–10] and multi-domain vertical alignment (MVA),[11–13] have been developed to meet the needs of consumers. Among all these driving modes, the vertical-alignment mode is especially more interesting due to its excellent contrast ratio in the normal direction. In general, the vertical alignment of LC molecules is achieved by using a polymer-type alignment layer. However, a polymer-type alignment layer requires the use of a high-temperature curing process in order to provide vertical alignment of the LC molecule and is not profitable in reference to commercialization. The achievement in uniformity pertaining to the polymer alignment layer of a large-sized panel display designed for over 2 m^2 in size for Gen8 LCD fabrication lines is also demanding and challenging. Recently, polyhedral oligomeric silsesquioxane (POSS)[14–22] nanoparticles dispersed in LC show uniform vertical alignment without the need for any further aligner on the substrates. However, to achieve multi-domain vertical alignment using POSS with high image quality in all viewing directions has not been proposed.

In this work, we stabilized LC directors in four azimuthal directions using surface polymer-stabilization (PS) technology[23–27] combined with the use of fine-patterned electrodes. In the process, LC was mixed with POSS and reactive mesogen at a proper weight-to-weight ratio, and the mixture was filled into the cell followed by UV light exposure under a sufficient applied electric field. As a result, we have achieved a new alignment-layer-free vertically aligned (NVA) device, which exhibits wide-viewing angle as well as fast response time.

2 Switching principle of NVA mode and its cell condition of fabricating process

The normalized transmittance of an LC cell in which a uniaxial LC medium exists between crossed polarizers can be defined as follows:

$$T/T_0 = \sin^2 2\psi(V)\sin^2[\pi d\Delta n_{\mathrm{eff}}(V)/\lambda], \qquad (1)$$

where ψ is a voltage-dependent angle between one of the transmittance axes of the crossed polarizers and the LC director, d is the cell gap, Δn_{eff} is the voltage-dependent effective birefringence of the LC medium, and λ is the wavelength of incident light. To achieve maximum transmittance at normal direction, $\psi(V)$ should be 45° and $d\Delta n_{\mathrm{eff}}(V)$ should be $\lambda/2$. In addition, the LC director should reorient in four different directions to minimize the viewing-angle dependence of $d\Delta n_{\mathrm{eff}}(V)$.

Figure 1 shows the top and side views of the electrode structures in the cell. The pixel electrode on the bottom substrate is fish-bone shaped with an electrode width (w) and distance between electrodes (l); in contrast, the top sub-

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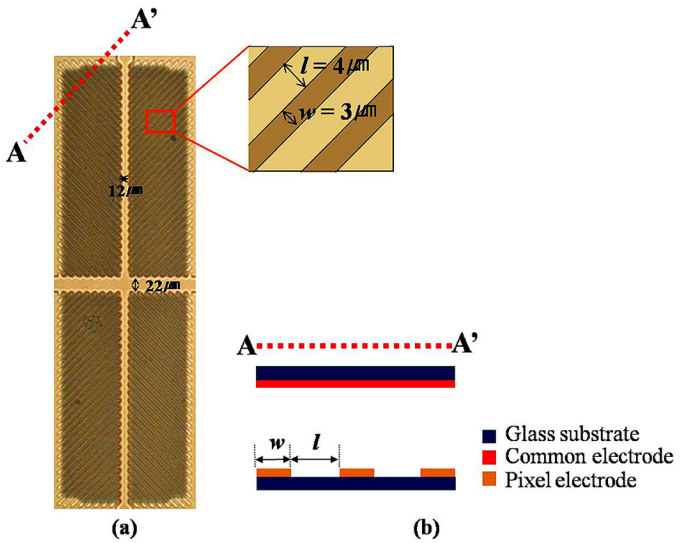

FIGURE 1 — (a) Top view of single-pixel structure in a test cell and (b) side view along cross-sectional line from A to A′.

strate has a plane ITO glass plate as a common electrode. With these electrode structures, in the voltage-off state, vertically aligned LC directors tilt downward along different electrode directions to form four domains in the voltage-on state, giving rise to the penetration of light under the crossed polarizers after full relaxation of the reorientation of the LC.

The LC, with negative dielectric anisotropy and birefringence values of –4.2 at 1 kHz and 0.079 at 589 nm, respectively, at 25°C was used in our research. The POSS (phenethyl-polyhedral oligomer silsesquioxane) of molecular size in the range of 1–3 nm was purchased from *SIGMA-ALDRICH*. The reactive mesogen (RM 257) used in this study was from *Merck* and polymerized by UV light exposure at the specific wavelength of 365 nm. The electrode width (w) and distance (l) between patterned electrodes with a fishbone structure were 3 and 4 μm, respectively, as shown in Fig. 1. The cell gap and retardation were maintained at 4 and 0.316 μm in the same manner.

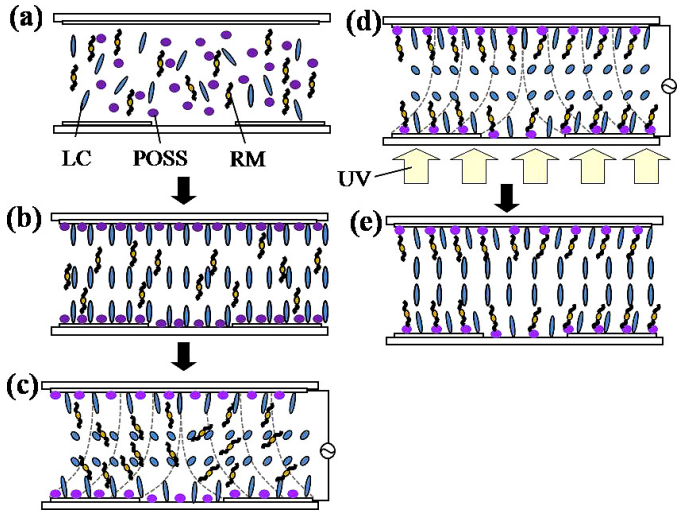

FIGURE 2 — Schematic fabricating process of NVA cell: (a) LC, POSS, and RM are uniformly distributed inside a cell. (b) POSS is diffused at both surfaces of the substrate, inducing vertical alignment of the LC. (c) A field is applied between the top and bottom electrodes to induce a surface tilt angle. (d) UV is exposed at a voltage larger than threshold. (e) Surface tilt angle is formed even without an applied voltage due to a fixed tilt angle by the polymerization of RM at both surfaces.

Figure 2 depicts the schematic fabrication process of an NVA cell. Initially, LC, POSS, and UV-curable RM were mixed in a fixed weight ratio of 1:0.1:0.001 and filled into a cell having a fishbone electrode structure by using the one-drop-filling (ODF) method. Once the mixture was filled into the cell, the POSS nanoparticles diffuse to both surfaces of the substrates and induced vertical alignment to the LC directors. Because the surfaces of both substrates are mainly a transparent electrode and indium-tin-oxide (ITO), the origin of diffusion of POSS to both substrate surfaces is possibly due to stronger POSS–surface interaction in contrast to POSS-LC interaction. Once the vertical alignment of LC is confirmed, a sufficient electric field larger than the threshold field (E_{th}) was applied to the sample cell to reorient the RM as well as the LC with a small tilt angle from the vertical direction and then simultaneously exposed by UV light with a specific intensity. As a result, the RM is polymerized on the POSS dispersed on the surfaces. Consequently, even without application of an electric field, the LC director has a specific tilt angle from the vertical alignment to form a multi-domain in the field-on state.

3 Experimental results and discussion

At first, we investigated the surface morphology of ITO and the patterned electrodes of the sample substrates to confirm the implementation by POSS and polymerized RM by using high-resolution field-emission scanning electron microscope (FE-SEM) (*Hitachi S-4300SE*). As indicated in the SEM images shown in Fig. 3(a), the surfaces of patterned electrodes and ITO substrates are sanitary without any significant roughness. However, as shown in Fig. 3(b), the FE-SEM image of UV-treated cell substrates at a magnification of 50,000× shows considerable surface roughness. By close analysis at a much higher magnification, it was found that the UV-cured substrates have randomly distributed and vertically elongated protrusion [see Fig. 3(c)] with an elongation height of about 50–100 nm. Furthermore, we observed that the SEM image actually resembles the schematic diagram (Fig. 2) and shows a surface morphology very similar to that of polymerized RM formed on the vertical-alignment layer.

Subsequently, we investigated the electro-optic characteristics of the NVA cell filled with POSS and RM mixed LC, before and after UV exposure to confirm the predetermined surface tilt angle on the polymerized RM POSS surfaces. Figure 4 shows macroscopic and microscopic polarizing optical microscopic (POM) images of the NVA cell in the voltage-off and voltage-on states. As shown in Fig. 4, for an initially good dark state, the NVA cell confirms

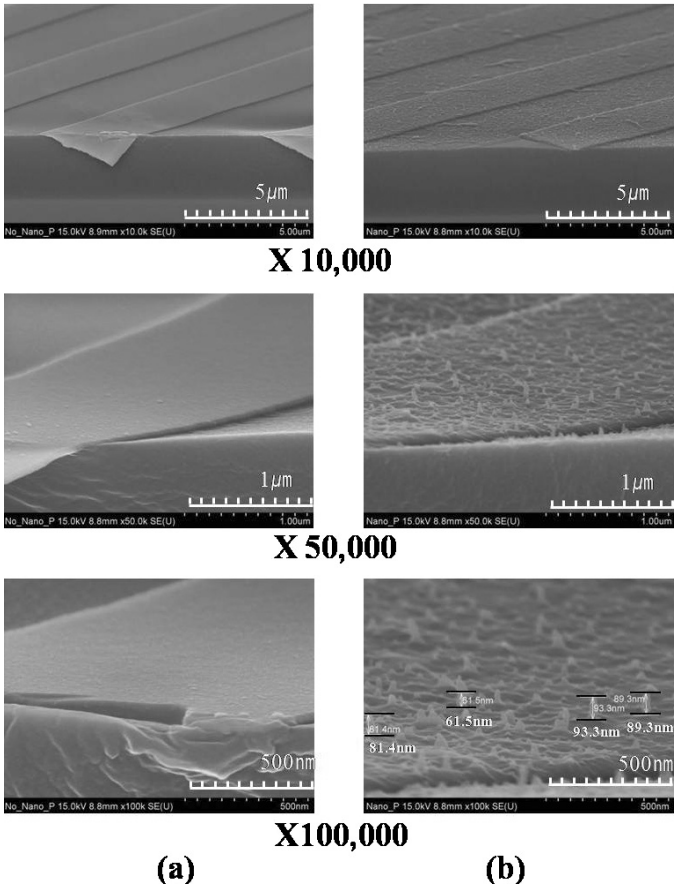

FIGURE 3 — SEM images of the surface morphology: (a) before and (b) after UV curing.

that the LC directors are vertically aligned by POSS nanoparticles. In the field-on state, most of the area in the cell becomes uniformly white and the switching from

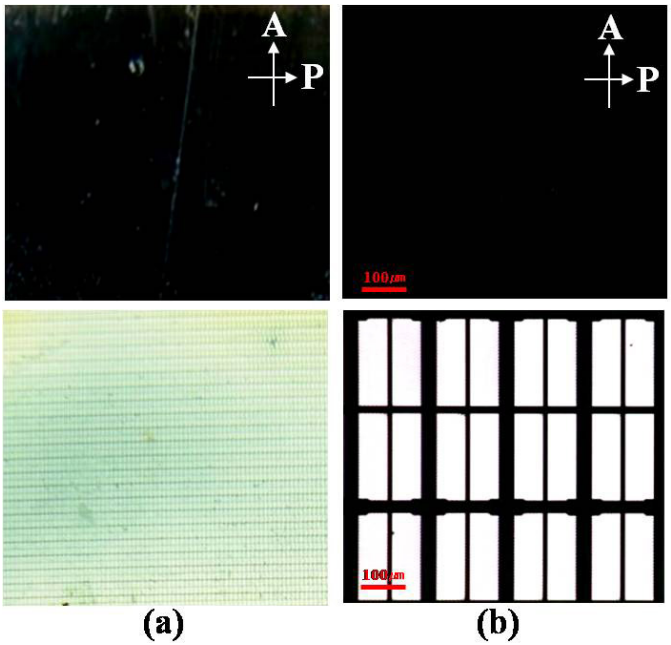

FIGURE 4 — (a) Macroscopic and (b) microscopic POM images in the dark and white state.

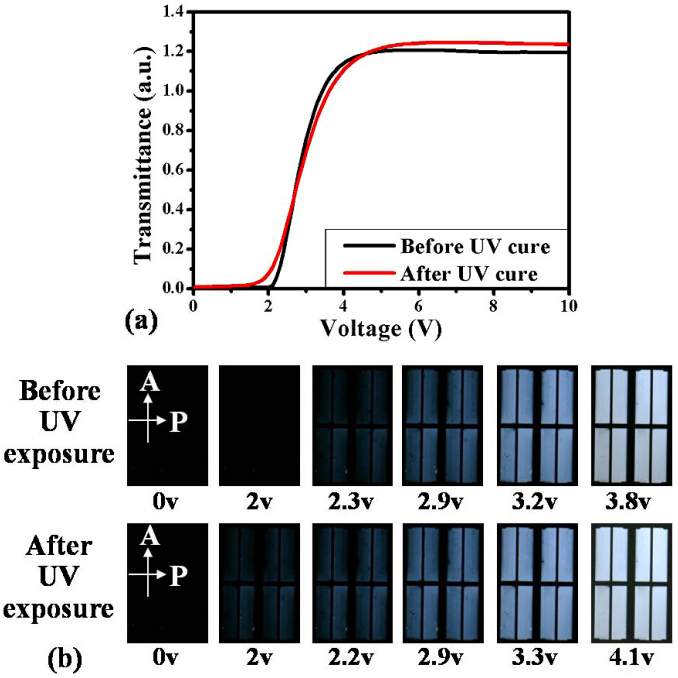

FIGURE 5 — (a) Comparison of voltage-dependent transmittance curves before and after UV curing in the NVA cell and (b) POM LC textures according to applied voltages. The UV-cured cell shows a lower threshold voltage than that in the UV-uncured cell.

the dark to the bright state was found to be reversible even after numerous successive switching cycles. It indicates that the anchoring force of LC molecules on a polymerized POSS surface is reasonably strong. Nevertheless, we have to admit that a few areas in the test cell were not found to be ideally dark which is possibly due to void dispersion of POSS nanoparticles on the substrate surface. As a result, to achieve uniform vertical alignment using POSS over the entire area in the cell is still a challenging issue.

Next, the voltage-dependent transmittance (V–T) characteristics of the NVA cell were measured before and after UV exposure, as shown in Fig. 5(a). As indicated, the UV-treated cell shows less-steep V–T curves with a reduction in V_{10} (voltage at which the transmittance changes by 10% from the maximum transmittance) from 2.3 to 2.2 V compared to a UV-untreated cell, which is associated with the existence of a surface pretilt angle less than 90°. Fur-

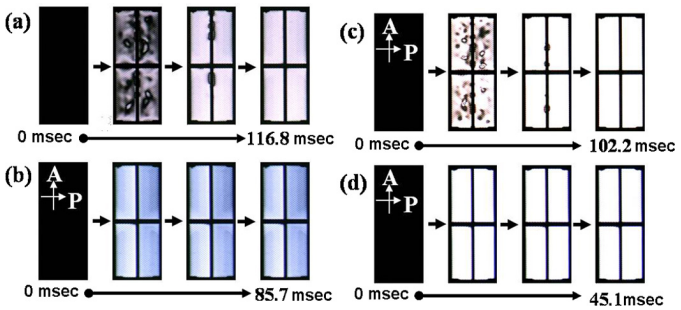

FIGURE 6 — Time-resolved LC textures at two different applied voltages V_{50} [(a) and (b)] and V_{90} [(c) and (d)] before [(a) and (c)] and after [(b) and (d)] UV curing in the NVA cell.

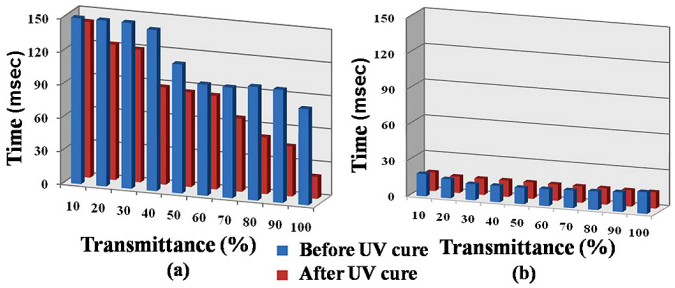

FIGURE 7 — Comparison of (a) rising and (b) decaying times according to the gray scale before and after UV curing in the NVA cell.

thermore, the level of light leakage slightly increased from 0.005 to 0.009 (in arbitrary units) in the UV-treated cell; again confirming the existence of the surface pretilt angle. Next, the electrically field-driven LC reorientation has been analyzed by the observation of microscopic images. As shown in Fig. 6(b), although the transmittance increases uniformly with an increase in applied voltage in both cells, the UV-cured cell shows a significant value of transmittance even at 2 V, unlike the UV-untreated cell and is in good agreements with the *V–T* curves.

Further, as shown in Fig. 7, time-resolved textures in a single pixel of the cell were investigated in order to confirm the surface tilt angle and stabilization of LC directors by the polymerized RM on POSS-dispersed surfaces. Two different voltages, V_{50} and V_{90} at which the transmittance changes by 50% and 90% from the maximum transmittance, respectively, were applied to the cell. Before UV treatment of the cell, the schlieren textures from collisions between LC molecules appeared as soon as the voltage is applied and then reached the final stabilized state of LC directors [see Figs. 6(a) and 6(c)]. However, the schlieren texture did not appear in any way in the UV-treated cell during the reorientation process of the LC directors. It indicates that such collisions between LC directors disappeared in the UV-treated cell by the polymerization on POSS surfaces. Besides, the relaxation time required to complete the reorientation of the LC director by an applied voltage is greatly reduced in the UV-treated cell. To compare the reorientation time of the LC directors between UV-untreated and UV-treated cells, the response times were measured for both the rising and decaying process for 10 gray levels, as shown in Fig. 7. Up until the fully bright state is reached, the UV-treated cell shows a rising time which is more than 2 times faster than that of the UV-untreated cell and also improves at all gray levels. In general, a higher surface tilt angle corresponds to a slower decaying time. But in our study, we found that the decaying time for both sample cells is almost the same, which indicates that the surface tilt angle does not greatly deviate from 90°. Overall, the results show the formation of pretilt angles of LC molecules by applying polymer stabilization techniques using UV-curable RM on a POSS surface.

4 Summary

VA–LCD having a multi-domain structure and fast response time without using a conventional polymer-type alignment layer is proposed. The LC is mixed with POSS nanoparticles and UV-curable monomer, for which the nanoparticles diffused at both the surfaces of substrates induce vertical alignment of the LC director along with a fixed surface pretilt angle on surfaces of the nanoparticle via polymerization by UV exposure under a sufficient applied voltage. The device has many advantages such as simple manufacturing process and cost-savings because the conventional alignment layer requires a thermal curing process at a high temperature of over 200°C and is no longer required for the present approach. We believe that this device is suitable for green-technology LCDs.

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