Photo-configurable embossed liquid crystal alignment layer with high azimuthal anchoring strength

Dowon Ahn,[1,5] Yong-Cheol Jeong,[2,5] Manhee Han,[3] Kuk Young Cho,[4] Seungsup Lee,[3] and Jung-Ki Park[1,*]

[1]*Department of Chemical and Biomolecular Engineering, KAIST, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea*

[2]*LCD R&D Center, Samsung Electronics, San#24 Nongseo-dong, Kiheung-gu, Yongin city, Kyeongki-do, 446-711, South Korea*

[3]*Department of Mechanical Engineering, KAIST, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, South Korea*

[4]*Division of Advanced Materials Engineering and Institute for Rare Metals, Kongju National University, 275, Budae-dong, Cheonan, Chungnam, 331-717, South Korea*

[5]*These authors contributed equally to this work*

[*]*jungpark@kaist.ac.kr*

Abstract: Herein we describe a photo-alignment layer of improved azimuthal anchoring energy comparable to conventional rubbing method. In order to address the inherent low anchoring stability of photo-alignment layer, we applied embossing technique to conventional photosensitive polymer film, based on the cinnamoyl photoreactive groups, to introduce physical micro-groove effect for additional anchoring energy. From this, 2.5 × 10^{-4} J/m^2 of azimuthal anchoring energy was achieved, which is considered as synergistic effect from both photoinduced chemical interaction and physical microgroove alignment. In this study, we conducted systematic study on change in anchoring energy as a function of both aspect ratio of embossed pattern and UV exposure dose. We also demonstrated fabrication of sophisticated multi-domain structure of LC cells and discussed theoretical interpretation through LC simulation.

OCIS codes: (230.3720) Liquid-crystal devices; (160.3710) Liquid crystals.

References and links

1. S. S. Sridharamurthy, K. D. Cadwell, N. L. Abbott, and H. Jiang, "A microstructure for the detection of vapor-phase analytes based on orientational transitions of liquid crystals," Smart Mater. Struct. **17**(1), 012001 (2008).
2. J. M. Brake, M. K. Daschner, Y. Y. Luk, and N. L. Abbott, "Biomolecular interactions at phospholipid-decorated surfaces of liquid crystals," Science **302**(5653), 2094–2097 (2003).
3. R. R. Shah and N. L. Abbott, "Orientational transitions of liquid crystals driven by binding of organoamines to carboxylic acids presented at surfaces with nanometer-scale topography," Langmuir **19**(2), 275–284 (2003).
4. L. Wei, J. Weirich, T. T. Alkeskjold, and A. Bjarklev, "On-chip tunable long-period grating devices based on liquid crystal photonic bandgap fibers," Opt. Lett. **34**(24), 3818–3820 (2009).
5. L. Z. Ruan, J. R. Sambles, and I. W. Stewart, "Self-organized periodic photonic structure in a nonchiral liquid crystal," Phys. Rev. Lett. **91**(3), 033901 (2003).
6. M. O'Neill and S. M. Kelly, "Photoinduced surface alignment for liquid crystal displays," J. Phys. D Appl. Phys. **33**(10), R67–R84 (2000).
7. J. van Haaren, "Wiping out dirty displays," Nature **411**(6833), 29–30 (2001).
8. M. Schadt, H. Seiberle, and A. Schuster, "Optical patterning of multi-domain liquid-crystal displays with wide viewing angles," Nature **381**(6579), 212–215 (1996).
9. J. H. Kim, M. Yoneya, and H. Yokoyama, "Tristable nematic liquid-crystal device using micropatterned surface alignment," Nature **420**(6912), 159–162 (2002).
10. P. Prompinit, A. S. Achalkumar, J. P. Bramble, R. J. Bushby, C. Wälti, and S. D. Evans, "Controlling liquid crystal alignment using photocleavable cyanobiphenyl self-assembled monolayers," ACS Appl. Mater. Interfaces **2**(12), 3686–3692 (2010).
11. H. K. Bisoyi and S. Kumar, "Liquid-crystal nanoscience: an emerging avenue of soft self-assembly," Chem. Soc. Rev. **40**(1), 306–319 (2010).
12. H. Qi and T. Hegmann, "Multiple alignment modes for nematic liquid crystals doped with alkylthiol-capped gold nanoparticles," ACS Appl. Mater. Interfaces **1**(8), 1731–1738 (2009).

#160771 - $15.00 USD Received 3 Jan 2012; revised 28 Jan 2012; accepted 2 Feb 2012; published 9 Mar 2012

13. S. R. Nersisyan, N. V. Tabiryan, D. M. Steeves, and B. R. Kimball, "The promise of diffractive waveplates," Opt. Photonic News **21**(3), 40–45 (2010).
14. M. Schadt, K. Schmitt, V. Kozinkov, and V. Chigrinov, "Surface-induced parallel alignment of liquid crystals by linearly polymerized photopolymers," Jpn. J. Appl. Phys. **31**(Part 1, No. 7), 2155–2164 (1992).
15. P. Chaudhari, J. Lacey, J. Doyle, E. Galligan, S. C. A. Lien, A. Callegari, G. Hougham, N. D. Lang, P. S. Andry, R. John, K. H. Yang, M. Lu, C. Cai, J. Speidell, S. Purushothaman, J. Ritsko, M. Samant, J. Stöhr, Y. Nakagawa, Y. Katoh, Y. Saitoh, K. Sakai, H. Satoh, S. Odahara, H. Nakano, J. Nakagaki, and Y. Shiota, "Atomic-beam alignment of inorganic materials for liquid-crystal displays," Nature **411**(6833), 56–59 (2001).
16. W. Schenck, D. H. Ko, and E. Samulski, "Liquid crystal alignment on polymer line gratings," J. Appl. Phys. **109**(6), 064301 (2011).
17. S. Park, C. Padeste, H. Schift, J. Gobrecht, and T. Scharf, "Chemical nanopatterns via nanoimprint lithography for simultaneous control over azimuthal and polar alignment of liquid crystals," Adv. Mater. (Deerfield Beach Fla.) **17**(11), 1398–1401 (2005).
18. D. Suh, S. J. Choi, and H. H. Lee, "Rigiflex lithography for nanostructure transfer," Adv. Mater. (Deerfield Beach Fla.) **17**(12), 1554–1560 (2005).
19. D. Ahn, Y. C. Jeong, S. Lee, J. Lee, Y. Heo, and J. K. Park, "Control of liquid crystal pretilt angles by using organic/inorganic hybrid interpenetrating networks," Opt. Express **17**(19), 16603–16612 (2009).
20. M. Schadt and H. Seiberle, "Optical patterning of multidomain LCDs," J. Soc. Inf. Disp. **5**(4), 367–370 (1997).
21. Y. Xia and G. M. Whitesides, "Soft lithography," Angew. Chem. Int. Ed. **37**(5), 550–575 (1998).
22. D. Ahn, Y. C. Jeong, S. Lee, and J. K. Park, "UV-driven in-plane rotation of a liquid crystal director in poly(vinyl cinnamate) films having microscale grooves," Opt. Lett. **35**(18), 3141–3143 (2010).
23. D. W. Berreman, "Solid surface shape and the alignment of an adjacent nematic liquid crystal," Phys. Rev. Lett. **28**(26), 1683–1686 (1972).
24. G. P. Bryan-Brown and I. C. Sage, "Photoinduced ordering and alignment properties of polyvinylcinnamates," Liq. Cryst. **20**(6), 825–829 (1996).
25. J. Stohr, M. G. Samant, J. Luning, A. C. Callegari, P. Chaudhari, J. P. Doyle, J. A. Lacey, S. A. Lien, S. Purushothaman, and J. L. Speidell, "Liquid crystal alignment on carbonaceous surfaces with orientational order," Science **292**(5525), 2299–2302 (2001).
26. R. Yamaguchi, Y. Goto, and S. Sato, "A novel patterning method of liquid crystal alignment by azimuthal anchoring control," Jpn. J. Appl. Phys. **41**(Part 2, No. 8A), L889–L891 (2002).

1. Introduction

Liquid crystals have found wide use in electro-optical fields, such as chemical and biological sensors [1–3], photonic devices [4–6] and of course liquid crystal displays (LCDs). Among those applications, LCDs utilize the optical properties of a specific state of liquid crystalline in the presence or absence of external electric field. In general, nematic liquid crystal molecules typically exhibit a preferred orientation with respect to a surface of alignment layer due to chemical and microscopic structural interactions. Since the quality of display device is highly influenced by an anisotropic ordering of LCs, it is significant to achieve uniformly controlled surface of thin film with environmental stability. For an alignment layer, rubbing of the thin film (usually polyimide) has been used for commercial devices up to dates due to relatively good anchoring energy as well as simplicity in procedure [7]. However, despite of aforementioned advantage of rubbing technique, it has an inevitable drawback of particle defects and electrostatic charge induced by the friction between the alignment layer and the rubbing pad, leading to considerable light scattering. Furthermore, mechanical rubbing is not a proper method to produce more complicated LC alignment layer including multi-domain structures for wide-viewing angle displays [8], orientational checker-board patterns for bistable or tristable displays [9], and other challengeable structures [10–13].

In line with these, as alternatives to the rubbing process, several featured works of noncontact approaches including photo-alignment [8,14], ion beam irradiation [15], and surface patterning [16] have been reported. Among them, patterned surface of thin film provides relatively high performance of LC ordering by its surface topology acting like a microgroove in rubbing method [17,18]. However, the surface patterning by using an embossing technique requires fine resolution of photolithography (usually sub-micron scale) for desirable property of anchoring energy. Moreover, sophisticated master mold is required to obtain multi-domain structure of LC alignment layer, resulting in high cost process. By contrast to embossing technique, the photo-alignment method, by which chemically anisotropic surface is generated, has drawn much attention due to its cost-effective fabrication process, and ease of its application to multi-domain structure without any contacting to alignment layer [8,19]. However, in spite of these potential advantages, the application of

#160771 - $15.00 USD Received 3 Jan 2012; revised 28 Jan 2012; accepted 2 Feb 2012; published 9 Mar 2012

photo-alignment method to the practical LCD is still rather limited because it suffers from alignment instability, image sticking, and relatively low anchoring energy [20].

Connection to these points, we present a photo-alignment layer of improved anchoring energy by combining the photo-sensitive film with embossing technique, of which the final orientation of LC molecules is configured by means of polarization direction of UV light. We believe that combining of photo-alignment layer with surface patterning provides simple and expandable method for multi-domain structure with enhanced stability of LC anchoring.

2. Preparation of the surface patterned photo-alignment layer

In order to prepare surface patterned photo-alignment layer, poly(vinyl cinnamate) (PVCi) solution, which is commonly used as the photoalignment layer based on (2 + 2)-cycloaddition of photodimerization [8], was cast on the glass substrate and embossed through solvent-assisted micro-molding (SAMIM) method, as schematically illustrated in Fig. 1 [21]. The SAMIM method is suitable to transfer physical topography from an elastomeric polydimethylsiloxane (PDMS) mold to a thermoplastic polymer film. The PDMS molds (Sylgard TM184, Dow Corning Co.) having various groove sizes were fabricated by casting a syrup of prepolymer onto silicon master of square-wave grating pattern prepared by conventional photolithography. Interestingly, contrary to no LC orientation on the surface of conventional PVCi film without UV exposure, the LC molecules were aligned planar to the surface patterned PVCi film without UV irradiation. From this, it is conjectured that the anchoring stability of pre-aligned LC molecules is expected to be improved by post-UV exposure; chemical interaction is additionally induced by anisotropically photodimerized cinamate groups. Since the anchoring energy of embossed alignment layer is considerably influenced by the aspect ratio of stripe pattern as well as its shape, in this report, we prepared four different master molds (having same shape and pitch, but different height of pattern) to fabricate the patterned PVCi alignment layers. The square-shaped master molds were fabricated by replicating the square-shaped photoresist microstructures with electroplating process. Briefly, the negative photoresist (SU-8 from MicroChem) microstructures were prepared using a conventional photolithography including sequential processes of a spin-coating of photoresist, UV exposing through chrome mask, and a developing. We could control the thickness of photoresist microstructures by modulating the rpm of spin-coater and generate the same period by taking same photomask in exposure step.

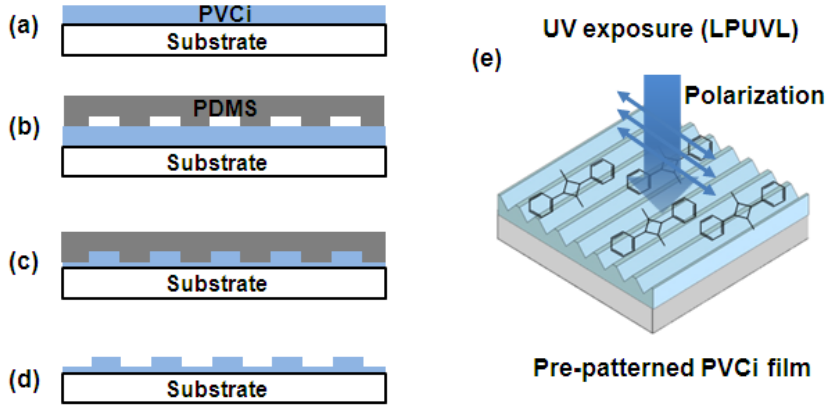

Fig. 1. Schematic illustration of the solvent-assisted micromolding method: (a) PVCi is spin-coated and baked. (b) The PDMS mold with the desired topography is swollen by the solvent and place on the PVCi film. (c) The micro-patterned PVCi solidifies as the solvent dissipates and evaporates. (d) The PDMS mold is removed to reveal the polymer pattern. (e) After the formation of relief structure on the alignment layer, irradiation of linear polarized UV light (LPUVL) generates anisotropic interactiosn between PVCi and LC interface with increase in photo-induced dimers. The generation of photo-induced dimers is perpendicular to LPUVL direction.

#160771 - $15.00 USD Received 3 Jan 2012; revised 28 Jan 2012; accepted 2 Feb 2012; published 9 Mar 2012

The detailed patterning procedures by using SAMIM method to form microgroove-like surface topology of the alignment layer are described in our previous work [22]; PVCi (Sigma-Aldrich Co.) powder was dissolved in cyclohexanone and the solution was spin-coated on a glass substrate, followed by thermal baking. An elastomeric PDMS mold was then wetted with an acetone that is a good solvent for PVCi, and placed on the surface of the PVCi layer. While the mold was maintained in conformal contact with the substrate, the solvent dissolved a thin layer of PVCi and after 5 minutes of solvent evaporation, PVCi was solidified to form relief structure with a pattern complementary to that on the surface of the mold. The width and height of the stripe pattern was measured by using atomic force microscopy (AFM), as depicted in Fig. 2. The measured groove widths were 2.03 μm (PTN1), 1.78 μm (PTN2), 2.11 μm (PTN3), and 1.88 μm (PTN4). The groove depths were 220 nm (PTN1), 386 nm (PTN2), 744 nm (PTN3), and 1.49 μm (PTN4), respectively. It revealed that the aspect ratio of patterns were 0.11 (PTN1), 0.22 (PTN2), 0.35 (PTN3), and 0.79 (PTN4), respectively, of which anchoring energy was increased monotonically with proportion to aspect ratio as expected from Berreman's report [23].

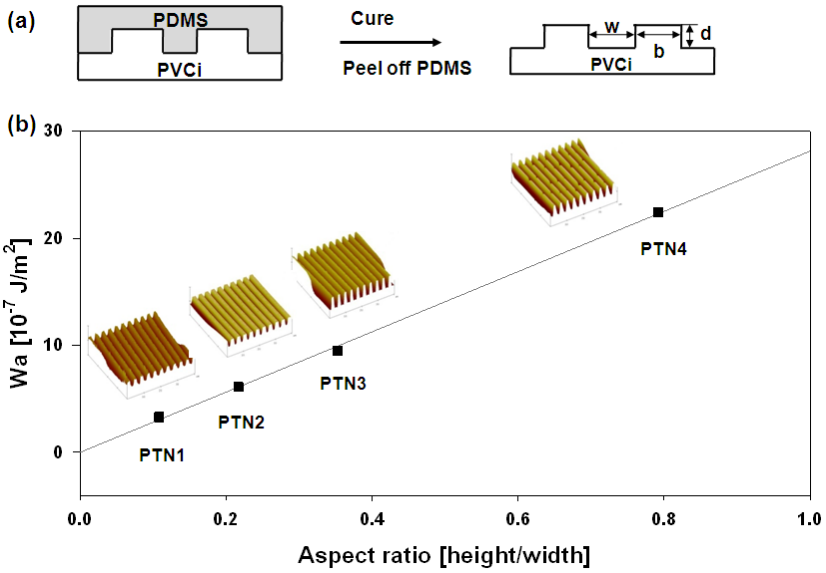

Fig. 2. Four different patterned PVCi alignment layers: (a) Feature sizes of the alignment layer. (b) AFM images of the patterned PVCi alignment layers and determined W*a* without UV irradiation (W*a*: azimuthal anchoring energy).

3. Synergistic effect on azimuthal anchoring stability

In order to explore synergistic effect of photo-alignment on anchoring stability, surface patterned PVCi film was exposed to linear-polarized UV light (LPUVL), of which polarization direction was perpendicular to the long axes of pre-aligned LC molecules (by the surface topology). This is because the direction of photo-induced (2+2)-cycloaddition of PVCi is perpendicular to LPUVL [14]. The irradiation was conducted by passing light from a 500 W high-pressure mercury arc (Oriel) through a UV linear dichroic polarizer (27320, Oriel) and a UV band-pass filter (59800, Oriel) onto the micropatterned PVCi alignment layer. The intensity of the UV irradiation, which was measured by using a UV detector (Delta OHM, HD 9021), was 2.3 mW/cm^2. The LC cell was assembled by homeotropic polyimide and aforementioned PVCi as a top and bottom alignment layer, respectively. The thickness of the LC layer was adjusted by using a polystyrene bead of 10 μm diameter. LC molecules (E7 from Merck) were injected into the cell via capillary force under isotropic phase, and the cell was gradually cooled to the temperature corresponding to nematic phase.

#160771 - $15.00 USD Received 3 Jan 2012; revised 28 Jan 2012; accepted 2 Feb 2012; published 9 Mar 2012

The azimuthal anchoring energy of LC was evaluated by measuring the twist angle of LC molecules, known as the cell rotation method [24]. For use in the cell rotation test, we fabricated the twisted planar cells by assembling rubbed polyimide film with non-patterned PVCi film as a top and bottom alignment layer, respectively, which excludes surface patterning effect. The cells were exposed to LPUVL and the azimuthal anchoring energy was evaluated as shown in Fig. 3. It turned out that the azimuthal anchoring energy was increased to 1.10×10^{-5} J/m^2 with UV exposure dose, of which value is 10 times lower than that of conventional rubbing method.

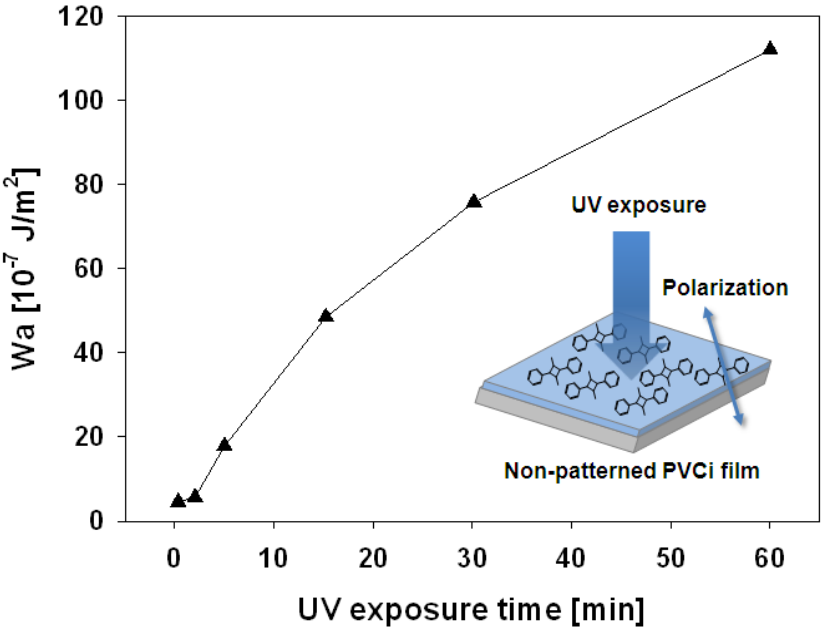

Fig. 3. Azimuthal anchoring energies of PVCi as a function of UV exposure dose.

In order to exploit aforementioned synergistic effect from photodimerization and surface topology, LPUVL was irradiated to surface patterned PVCi film as shown in Fig. 4. The initial azimuthal anchoring energies that are attributed only to topological effect of the patterned surface, and the other points represent azimuthal anchoring energies arising from both contribution of chemical anisotropic interaction and topological effect. Recent studies pointed out that chemical interactions driven by the realignment of polymer chains during rubbing process are particularly responsible for LC alignment rather than the surface topography [25]. In our studies, chemical interaction effect also seems to be more important for LC orientation as supported in Fig. 4. It shows that only a small dose of UV exposure (69 mJ/cm^2, 5 min) can dramatically increase azimuthal anchoring energy of the patterned PVCi alignment layer. In addition, the total azimuthal anchoring energy is quite much higher than the value obtained from simple addition of each contribution. In the case of PTN4, highest aspect ratio, the azimuthal anchoring energy of 1.75 ~2.74×10^{-6} J/m^2 from surface topography in conjunction with that of 1.10×10^{-5} J/m^2 from chemical interaction of PVCi (UV exposure dose: 8 J/cm^2) could create with synergy high azimuthal anchoring energy of 2.49×10^{-4} J/m^2. Although the mechanism on the synergetic effect is not clearly understood at the moment, this value is actually quite close to the azimuthal anchoring energy available from the current rubbing method.

#160771 - $15.00 USD Received 3 Jan 2012; revised 28 Jan 2012; accepted 2 Feb 2012; published 9 Mar 2012

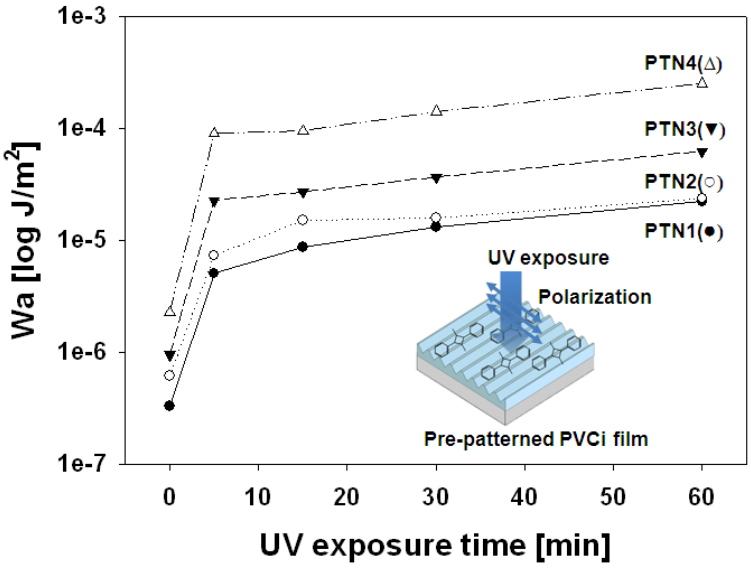

Fig. 4. Results of change in azimuthal anchoring energy of surface patterned PVCi as a function of UV exposure dose.

4. Multi-domain structure of LC alignment

To demonstrate the versatility our new patterned PVCi alignment layer to the delicate LC control, we established multi-domain structure of LC alignment by controlling the azimuthal anchoring energy of the alignment surface. Before experiment, we conducted theoretical expectation to conjecture the required change in azimuthal anchoring energy forming twist nematic structure. Figure 5 represents the theoretical result between the anchoring strength and the twist angle of LC calculated for the twisted nematic LC cell of which two alignment surfaces have a finite and an infinite anchoring energy [26]. The angle between two easy axes of the substrate is 90°. The free energy per unit area in the twisted nematic LC cell becomes minimal, when the relation is satisfied as shown in Eq. (1).

$$F = \frac{1}{2} K_{22} \frac{\Phi_t^2}{d} + \frac{1}{2} Wa \sin^2(\Delta\Phi) \qquad (1)$$

Where, K_{22} is the twist elastic constant (6.5×10^{-12} N, E7), Φ_t is the twist angle, d is the thickness of the LC layer (10 μm), and W_a is the azimuthal anchoring energy. This theoretical consideration indicates that the twist angle can be changed from 0° to 90°, if the azimuthal anchoring energy increases by a factor of two. Moreover, the LC director on the weak anchoring surface becomes parallel to the easy axis of the strong anchoring surface on the counter substrate, when W_a is smaller than K_{22}/d.

#160771 - $15.00 USD Received 3 Jan 2012; revised 28 Jan 2012; accepted 2 Feb 2012; published 9 Mar 2012

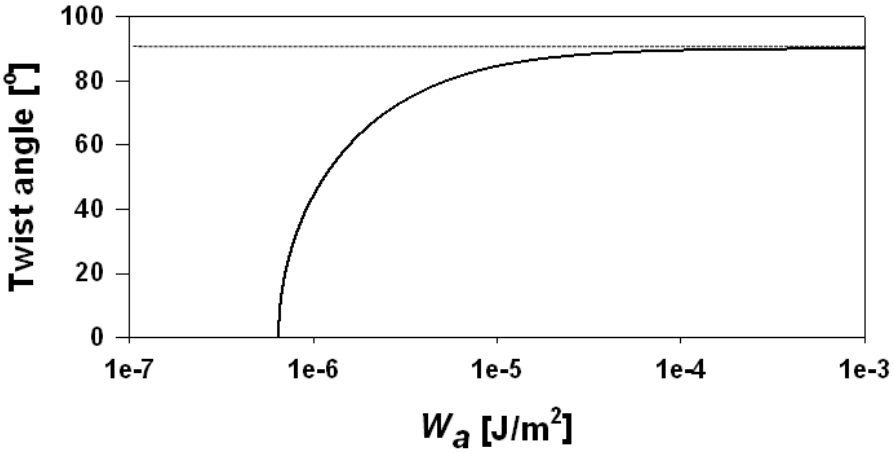

Fig. 5. The theoretical relationship between W*a* and *Φt*, denoted as solid line. (note that dash line indicates 90 degree of twist angle)

In order to elucidate the theoretical expectation, the patterned LC cell was fabricated with the following process: The patterned PVCi surface was partly irradiated with polarized UV light (500W high pressure mercury arc, Oriel) using a photomask to generate multi-domains having different anchoring energies. A uniformly rubbed PI surface with strong anchoring of more than 1×10^{-4} J/m^2 was then produced as a counter alignment surface. The LC was in-filled between the patterned PVCi and the PI substrates as schematically shown in Fig. 6(a). Figure 6(b) shows the checker-board pattern of photomask used in this study where the size of each square was 100 μm. In this report, we present the result of the patterned LC alignment having PTN1 (lowest anchoring energy) in Fig. 6(c), observed by a polarization microscope after 1hr UV irradiation. The anchoring strength of the unexposed surface was about 2.23 ~4.38×10^{-7} J/m^2. The anchoring strength increased with the exposure time and reached to about 2.24×10^{-5} J/m^2 when the side-chains of PVCi were sufficiently photo-dimerized. The twist angle was consistent with the predicted value obtained from theoretical relationship between anchoring energy and twist angle, and LC molecules were twisted about 0° and 87.5°. The twist angle can also be controlled by adjusting the UV irradiation time, in other words, by regulating the anchoring of the patterned PVCi surface.

#160771 - $15.00 USD Received 3 Jan 2012; revised 28 Jan 2012; accepted 2 Feb 2012; published 9 Mar 2012

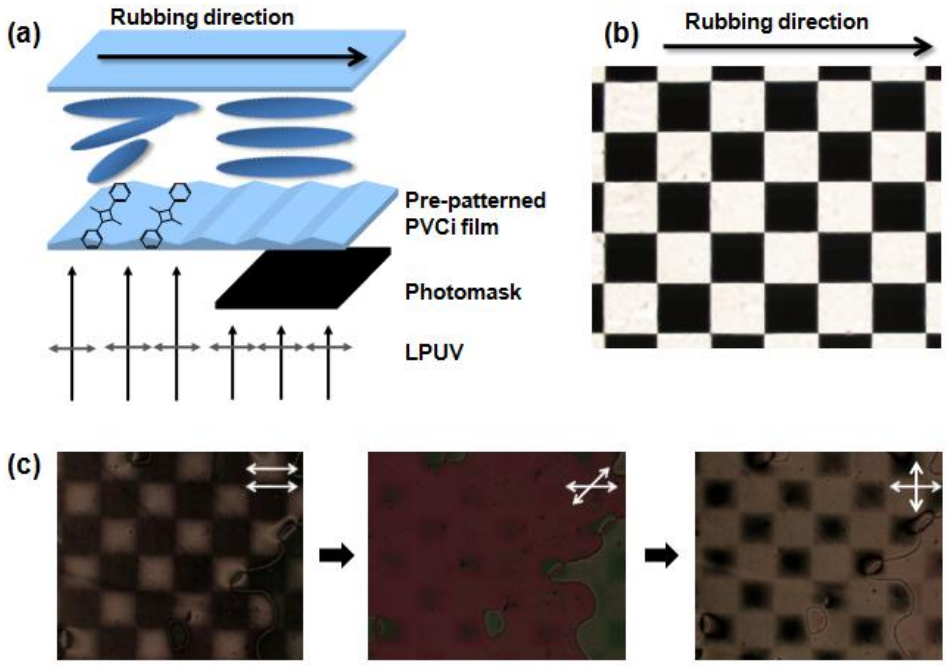

Fig. 6. The LC alignment patterning by using anchoring control. (a) Configuration of LC cells fabricated with patterned PVCi alignment layer. (b) Micrographs of the photomask used in this study. (c) Optical microscope photograph of the patterned LC cell between crossed polarizers. The size of each square is 100 μm. Double-headed arrows show the directions of polarizer and analyzer.

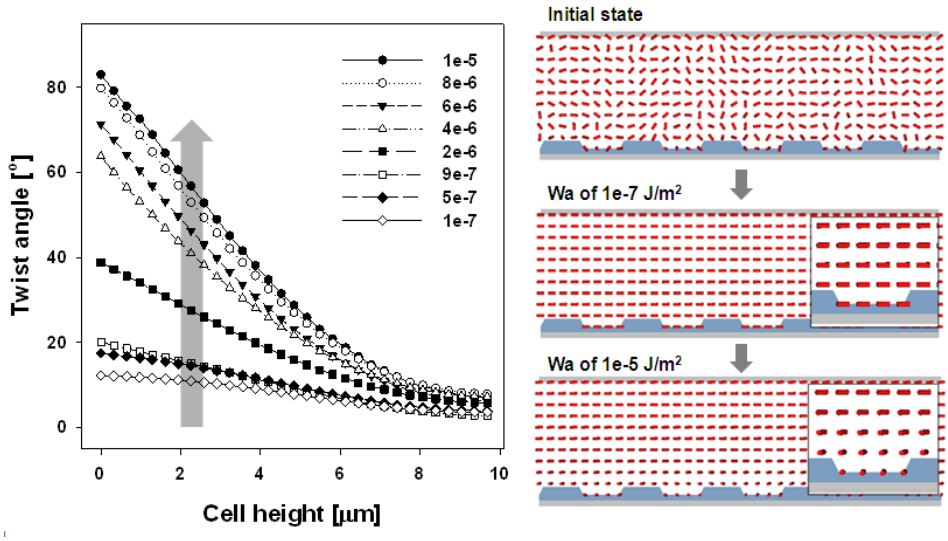

Fig. 7. LC simulation of effective twist angle of LCs between alignments as a function of different azimuthal anchoring energies, correlating well with experimental result.

Figure 7 also supports the experimental result through LC simulation by using commercial software of TechWiz LCD®. The LC molecules between alignment layers of twisted nematic mode were distributed randomly and then spontaneously aligned to minimize the entropy. (note that simulation was conducted with 3 dimensional space, but the cross-section is only presented in this report.) It shows that the LC molecules at bottom layer were rotated in lateral

#160771 - $15.00 USD Received 3 Jan 2012; revised 28 Jan 2012; accepted 2 Feb 2012; published 9 Mar 2012

direction as the anchoring energy of bottom alignment layer was increased, where the cross-sectional distributions of LC molecules are presented in Fig. 7. In detail, the LC molecules at bottom are aligned with similar direction of top alignment layer when the anchoring energy of bottom alignment is not high (10^{-7} J/m^2). However, the LC molecules have almost twisted nematic structure as the anchoring energy of bottom alignment layer is increased by a factor of two, which is well correlated with the experimental result.

5. Conclusions

The patterned PVCi alignment layers were fabricated by SAMIM method. The photo-dimerization process of PVCi enabled the patterned PVCi alignment layer to generate synergetic contribution of chemical interactions to the azimuthal anchoring of LC. It is confirmed that both the surface topography and the chemical interaction are responsible for the LC alignment and the synergetic effects can increase the azimuthal anchoring energies of LC cell very significantly, which results in a high azimuthal anchoring energy comparable to the value obtainable from the conventional rubbing method. In addition, we demonstrated that the multi-domain structure of the patterned PVCi LC cell can be successfully prepared by using our surface patterned PVCi alignment layer.

Acknowledgments

D. Ahn and Y.-C. Jeong contributed equally to this work. This research was supported by a grant from the Center for Nanostructured Materials Technology (code#: 2011K000217) under the 21st Century Frontier R&D Programs of the Ministry of Education, Science, and Technology of Korea as well as LG Chem. LTD.

#160771 - $15.00 USD Received 3 Jan 2012; revised 28 Jan 2012; accepted 2 Feb 2012; published 9 Mar 2012