Alignment of a Nematic Liquid Crystal on Nano-Grooved Material

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ABSTRACT: We demonstrate the alignment characteristics of a nematic liquid crystal on the surface of a nanoimprinted material that is a functionally graduated composite suitable for the alignment of a liquid crystal on a groove surface processed by nanoimprinting lithography. With the electro-optic characteristics shown in twisted nematic and in-plane switching modes, the potential liquid crystal applications are examined. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 325–329, 2011

Key words: liquid crystal display; nanoimprint lithography; LC alignment

INTRODUCTION

In general, nano-sized patterns on substrates can be obtained by direct photolithography, which is limited by diffraction when the pitch is finer than under 100 nm. Alternatively nano-patterns can be made indirectly by nanoimprinting lithography (NIL) with a mold that can be made by electron beam, ion beam, X-ray beam, and scanning probe tips using atomic force microscopy.[1–5] NIL has been applied to various areas of electronics, photonics, and magnetic device applications, such as nanoelectronic devices, thin-film transistors, organic lasers, organic electro luminescent displays, and magnetic disc. We expect that NIL can be applied to several new applications because it can produce nano-size patterns easily and simply with both a high-throughput and high precision.[6–16]

Liquid crystal displays (LCDs) are operated by controlling electrically the retardation of LCs, the multiplication of birefringence and thickness of the LCs, which are interposed between two polarizer substrates. LCs are anisotropic fluids whose thermodynamic properties are intermediate between those of the isotropic liquid and the three-dimensional positionally ordered crystal.[17,18] Uniform alignment of an LC on a substrate surface is important in LC technology as misalignment produces light leakage in the dark state. Several homogenous LC alignment methods have been proposed through various routes but at present the best LC surface alignment in the LCD industry is being obtained by the rubbing method, which achieves higher LCD stability through the high thermal stability caused by a high LC anchoring energy. However, there are several problems with the method, such as static electricity, debris, and fine scratches on the LC alignment layer generated from strong contact between the rubbing cloth and the substrate surface. This is a crucial issue in the design of next generation displays with higher resolutions. Surface grooves with a suitable pitch and depth are effective in aligning LCs.[19,20] NIL can generate these grooves with a stable and precise pitch so as to lead to good LC alignment. Thus, NIL enables us to precisely control the direction of surface anisotropy and the surface anchoring strength through control of the pitch and depth on a mold, which is hardly possible in the conventional rubbing process. Also we can readily obtain optically excellent mutidomain shapes in a pixel of an LC panel and nematic LC bistability[21,22] by the NIL approach. However, in spite of its evident advantages the NIL method has not been applied much to LC alignment technology so that analysis of the capabilities for LC alignment of nano-sized grooves created by NIL is inadequate. Another issue to be resolved in the promotion of the LC applications of NIL is the choice of appropriate material, which should have good imprinting characteristics under lower pressure and

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temperature and good LC alignment characteristics with high anchoring energy. The optimization of the imprinting conditions, such as imprinting pressure, temperature, and time in NIL technique with a given choice of LC alignment material is also important to permit exact transfer of the mold groove patterns into the film, with optimization of the baking conditions for a good imprinting.

A material for the application of NIL to the fabrication of liquid crystal devices has been developed. For the fabrication of liquid crystal devices using the NIL process, an LC alignment material suitable for NIL treatment is required. So the surface layer of this material must have the property of strong LC anchoring and the bulk material must be soft enough for NIL treatment. So we have proposed a hybrid type functionally graded material tailored for LC alignment.[23,24] The material, composed of a polyimide, a polyester amic acid (PEA), and an epoxy resin (ER), perfectly fulfills the property requirements of an LC alignment material suitable for NIL treatment.

In this article, we report the alignment characteristics of a nematic liquid crystal on the grooved surface of the selected material through the electro-optic characteristics of twisted nematic (TN) and in-plane switching (IPS) modes. In addition, the material can be used as a multifunctional layer combining the function of an LC alignment layer with the function of an overcoat layer to flatten uneven color filters in the IPS mode which needs electrode only at one substrate.

EXPERIMENTAL PREPARATION

We used polymethylmethacrylate (PMMA) as an LC alignment layer to test the LC alignment capability of the nano-sized groove pattern created by the NIL process because, PMMA with its weak polar anchoring may be a border line case of suitability for LC alignment by NIL.

In typical experiments, PMMA having a molecular weight of 2,00,000 g/mol, a thermoplastic material was used for LC alignment. The thickness of the PMMA film was in 300–400 nm produced by a 15 sec treatment in a spinner at 2500 rotations per minute. A new polyimide material was spun on a general slide glass with dimensions of 2 × 3 cm. It was a hybrid type material (HTM) consisting of PEA and a kind of ER with solvents of N-Methylpyrrolidone/Ethylene glycol butyl ether/γ-Butyrolactone = 55/35/10 as shown in Figure 1. After spin coating, the substrate with the new polymer film was baked in a hot plate at 100°C for 5 min to remove solvents and then prebaked on a hot plate at 165°C for 10 min to complete the ER crosslinking reaction. The post baking for the polyimidization reaction was performed for 30 min at 220°C on hard and flat metal planks which supported the sample in imprinting equipment. The thickness of the new polymer film was in the range 800–1000 nm after treatment for 20 s in a spinner at 3000 rotations per minute.

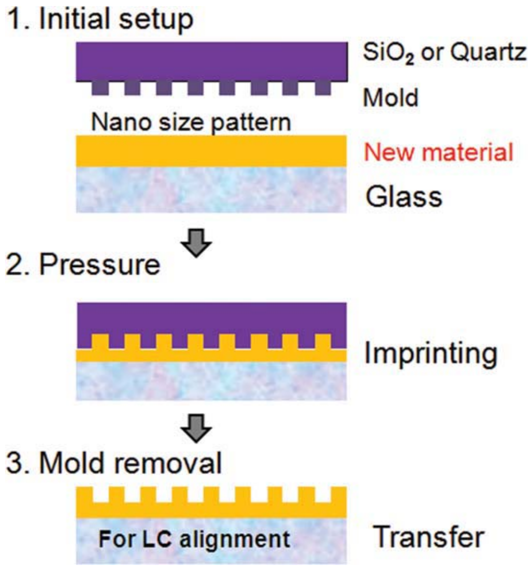

Figure 1 Simple nanoimprinting process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 1 shows a nanoimprinting process use in the experiments. The HTM and PMMA films were pressed under 10 MPa for 5 min at 200°C in a mold with an imprinting-machine (X-200-NV, SCIVAX). Subsequently, it was cooled down to below the glass transition temperature and separated. Figure 2 illustrates the pitch and the height of the patterns on the HTM substrate transferred from the mold, which are 200 and 110 nm, respectively. The mold patterns are clearly imprinted into the film having the correspondence as the mirror image each other. Therefore, we know that HTM film shows excellent capability as a nanoimprinting material.

EXPERIMENT AND RESULTS

Anchoring energy

Surface anchoring properties are important and interesting parameters in both basic and applied physics. Many reports about the properties of LC surfaces have been presented in many science journals and proceedings in the past ten years. We give here an outline of our recent theoretical treatment of LC alignment on surface grooves.[22,25] The geometry of the one-dimensional alignment direction imprinted by NIL can be described by

$$z = A\sin(qx), \tag{1}$$

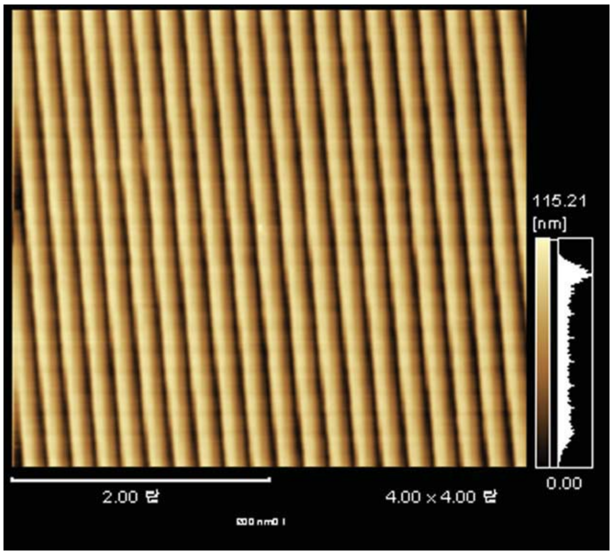

Figure 2 AFM image of one-dimensional linear groove pattern on the HTM film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where A is the amplitude of the modulations and q is the wave number defined as $q = 2\pi/\lambda$ (λ is the groove pitch). The Frank-Oseen free energy of a nematic liquid crystal is described as

$$F = \frac{1}{2}\int (K_1(\vec{\nabla}\cdot\vec{n})^2 + K_2(\vec{n}\cdot\vec{\nabla}\times\vec{n})^2 + K_3(\vec{n}\times\vec{\nabla}\times\vec{n})^2)dr, \quad (2)$$

where K's are elastic constants and $n^{\rightarrow}$ is the LC director. To find stable states of the LC director at bulk, with the surface boundary condition of eq. (1), the Euler-Lagrange equation with some manipulation is applied to eq. (2). Then we can obtain an expression for the azimuthal anchoring energy of this system in the form

$$W = \frac{1}{2}\sqrt{K_1}\sqrt{K_3}A^2q^3. \quad (3)$$

The LC material used in this experiment was type ZLI-2293 supplied by Merck. Here, chiral dopant was not used. The values of K_{11}, K_{22}, and K_{33} of this LC material are 12.5×10^{-12}, 7.3×10^{-12}, and 17.9×10^{-12} Pa, respectively. Thus, the anchoring strength of the LC cell with the groove pattern shown in Figure 2 becomes $\sim 2.8{\times}10^{-3}$ N/m from eq. (3).

To check whether this value is right or not, we measured directly the surface anchoring strength by determining optically the angle of deviation of the LC from the easy axis at a twisted LC state from the torque balance equation. Generally the total free energy per unit area, F_t can be expressed as the sum of the bulk elastic energy, F_b and the surface anchoring energy, F_s as follows:

$$F_t = F_b + F_s, \quad (4)$$

where

$$F_b = \frac{K_{22}}{2d}\left(\phi_r - \frac{2\pi d}{p}\right)^2 \text{ and } F_s = \frac{1}{2}W_a\sin^2\Delta\phi.$$

Here, K_{22} is the twist elastic constant, p is the chiral pitch of the LC, d is the cell thickness, ϕ_r is the actual twist angle, and $\Delta\phi$ is the angle at which the surface of the LC deviates from the easy axis. From eq. (4), the surface azimuthal anchoring strength, W_a can be written by

$$W_a = \frac{2K_{22}}{\sin(2\Delta\phi)}\left(\frac{\phi_r}{d} - \frac{2\pi}{p}\right) = \frac{2K_{22}}{\sin(\phi_e - \phi_r)}\left(\frac{\phi_r}{d} - \frac{2\pi}{p}\right). \quad (5)$$

Thus, if we can obtain the LC deviation angle, $\Delta\phi$, the surface anchoring strength can be determined uniquely. To find the LC deviation angle, we used a rotating polarizer method with a single-wave source.[26] Then, the measured anchoring energy was $\sim 8.7{\times}10^{-4}$ N/m. This value is three times lower than would be expected from eq. (3). It may be caused from polar anchoring because eq. (3) is a result driven from an assumption that the polar anchoring is extremely strong. However, in practice it has a finite value. Nevertheless, it is sufficiently strong to obtain LCDs with useful electro-optical characteristics.

Electro-optic characteristics

Figure 3 shows the microscopic optical images of a dark state and a bright state in TN and IPS LC cells made of nano-sized groove patterns on HTM and PMMA film substrates. The images in Figure 3 show very uniform darkness and brightness, indicating that the nano-size grooves in this system succeed in aligning the LC molecules well. One of the most important issues in LC alignment by NIL is pretilt angle control. However, we can know when the pretilt angle of an LC cell with a PMMA alignment layer was nearly zero because in the dark state of TN cells under the influence of an electric field, and given that the cells were fabricated under several imprinting conditions, discrination lines were shown in the all cells. Therefore, PMMA may be used only in the IPS mode which does not require a pretilt angle. On the other hand, the pretilt angle of an LC cell with HTM alignment layer treated by NIL, might not be zero because we could not find any discrination lines in the dark state under the

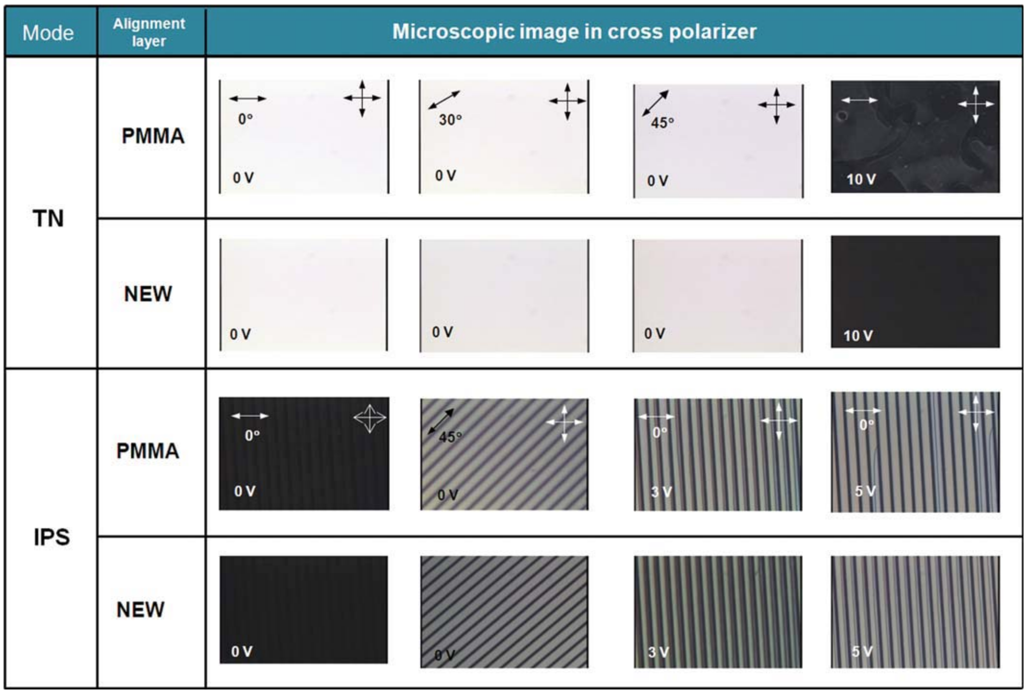

Figure 3 Microscopic images of TN and IPS cells with nano-sized groove pattern on the PMMA and HTM film substrates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

influence of an electric field in a TN cell. Perhaps, this result may be due to the nature of the polyimide in HTM film in raising the LC. The addition of a hydrophobic side chain into the polyamic acid, which has been used for the attainment of higher LC pretilt angles, may be a useful method to get higher LC pretilt angle in NIL.

Color filter overcoat

The above ideas can be applied to produce more effective overcoat layers on the color filters in LCDs. These color filters are layers of functional materials on the surface of a substrate which have three-primary colors of red, green, and blue. Figure 4 shows the basic structure of color filter glass in LCD panels, which is constructed of a glass substrate with a Cr-based black matrix and three colorant films in the specific subpixels. Generally, in the case of the color filter glass of the IPS mode which does not need electrode, to protect and flatten the color filter films, the color filters are covered by an overcoat layer which can also improve the optical transmittance. Also a polyimide layer should be coated on it to align the LCs in an additional process as shown in Figure 4(a).

HTM is a functionally separated material of which the bulk layer is suitable for NIL treatment and also for use as a color filter overcoat, whilst the surface layer functions as an LC alignment layer because the polyimide of the HTM components is distributed over the surface due to its lower surface free energy, compared with other components. Thus, if the HTM is used as the color filter overcoat, the process for coating the polyimide can be skipped as shown in Figure 4(b). As a result, the material can be used as a multifunctional layer combining the function of the LC alignment layer and the function of an overcoat layer to flatten uneven color filters in IPS mode, which makes the material very cost effective.

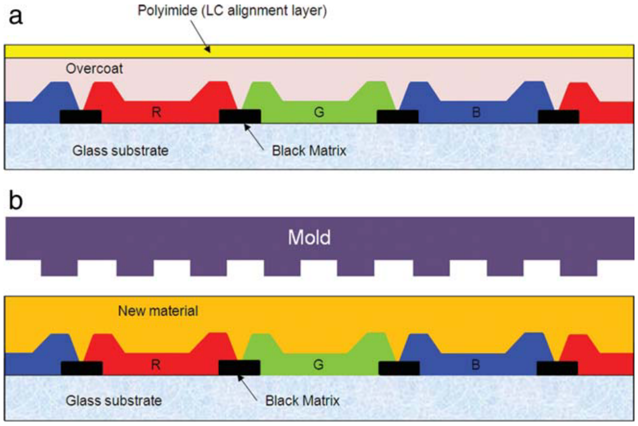

Figure 4 The basic schematic the color filter glass substrate with (a) the conventional overcoat and (b) the material having simultaneous functions of LC alignment and as a color filter overcoat. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSION

We demonstrate alignment characteristics of a nematic liquid crystal on the groove surface of the material through the electro-optic characteristics of TN and IPS modes. LC cells using this material show excellent electro-optic characteristics. In addition, the material can be used as a multifunctional layer combining the function of LC alignment layer and the function of an over-coat layer to flatten uneven color filters in the IPS mode which needs electrode only at one substrate. As a result, this material shows excellent capability, through its compatibility with both NIL processing and LC alignment.

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References

1. Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. Appl Phys Lett 1995, 67, 3114.
2. Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. Science 1996, 272, 85.
3. Khang, D.-Y.; Yoon, H.; Lee, H. H. Adv Mater 2001, 13, 749.
4. Li, M.; Chen, L.; Chou, S. Y. Appl Phys Lett 2001, 78, 3322.
5. Behdani, M.; Keshmiri, S. H.; Soria, S.; Bader, M. A.; Ihlemann, J.; Marowsky, G.; Rasing, T. Appl Phys Lett 2003, 82, 2553.
6. Wang, J.; Sun, X.; Chen, L.; Chou, S. Y. Appl Phys Lett 1999, 75, 2767.
7. Berggren, M.; Dodabalapur, A.; Slusher, R. E.; Timko, A.; Nalamasu, O. Appl Phys Lett 1998, 72, 410.
8. Mcclelland, G. M.; Hart, M. W.; Rettner, C. T.; Best, M. E.; Carter, K. R.; Terris, B. D. Appl Phys Lett 2002, 81, 1483.
9. Kagajyo, T.; Fujibayashi, K.; Shimamura, T.; Okada, H.; Onnagawa, H. Jpn J Appl Phys 2005, 44, 578.
10. Hayden, O.; Dickert, F. L. Adv Mater 2001, 13, 1480.
11. Cheng, X.; Guo, L. J.; Fu, P.-F. Adv Mater 2005, 17, 1419.
12. Austin, M. D.; Chou, S. Y. Appl Phys Lett 2002, 81, 4431.
13. Guo, L. J.; Krauss, P. R.; Chou, S. Y. Appl Phys Lett 1997, 71, 1881.
14. Pisignano, D.; Persano, L.; Visconti, P.; Cingolani, R.; Gigli, G.; Barbarella, G.; Favaretto, L. Appl Phys Lett 2003, 83, 2545.
15. Cheng, X.; Hong, Y. T.; Kanicki, J.; Guo, L. J. J Vac Sci Technol B 2002, 20, 2877.
16. Wu, W.; Cui, B.; Sun, X. Y.; Zheng, W.; Zhuang, L.; Kong, L. S.; Chou, S. Y. J Vac Sci Technol B 1998, 16, 3825.
17. Collings, P. J.; Hird, M. Introduction to Liquid Crystals; Taylor&Francis: London, 1997.
18. De Gennes, P. G.; Prost, J. The Physics of Liquid Crystals; Clarendon: Oxford, UK, 1993.
19. Berreman, D. W. Phys Rev Lett 1972, 28, 1683.
20. Berreman, D. W. Mol Cryst Liq Cryst 1973, 23, 215.
21. Gwag, J. S.; Kim, J.-H.; Yoneya, M.; Yokoyama, H. Appl Phys Lett 2008, 92, 153110.
22. Gwag, J. S.; Fukuda, J.; Yoneya, M.; Yokoyama, H. Appl Phys Lett 2007, 91, 073504.
23. Gwag, J. S.; Oh-e, M.; Yoneya, M.; Yokoyama, H.; Satou, H.; Itami, S. J Appl Phys 2007, 102, 063501.
24. Gwag, J. S.; Oh-e, M.; Kim, K.-R.; Yoneya, M.; Yokoyama, H.; Satou, H.; Itami, S. Nanotechnology 2008, 19, 395301.
25. Fukuda, J.; Gwag, J. S.; Yoneya, M.; Yokoyama, H. Phys Rev E 2008, 77, 011702.
26. Saitoh, Y.; Lien, A. Jpn J Appl Phys 2000, 39, 1743.