Bistable nano-structured photoalignment surface by nanoimprint lithography

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***Abstract* —** A novel nano-structured photoalignment surface is proposed and demonstrated. Such alignment surface has bistable azimuthal alignment directions for the liquid crystal molecules. The new alignment surface has a structure of stacking a photo-polymerizable photoalignment polymer on top of a nano-sized groove surface. The photoalignment polymer and groove surface have different azimuthal alignment directions but the same azimuthal anchoring energies. The fabrication of the nano-sized groove is based on nano-imprint lithography. Hence, the size and depth are controllable, where no random process is involved. The alignment surface is robust, stable, reliable, reproducible and suitable for mass manufacturing. Such alignment surface can be applied to fabricate a π/2 bistable twisted nematic (π/2-BTN) display which has better optical performances than the traditional π-BTN display.

Keywords *— bistable, nanostructured, photoalignment, nanoimprint.*

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Nano-structured alignment surfaces for liquid crystal (LC) alignment have been investigated for more than a decade.[1–6] This alignment surfaces can form nano-sized domains with different alignment properties, and hence it is attractive to researchers and manufacturers. For example, such alignment surfaces can generate arbitrary alignment directions and pretilt angles, especially in the range of 30°–80°.[5,6] The nano-structured alignment surfaces can be applied in many applications, such as bistable display devices,[7] fast switching display devices [8] and tunable liquid crystal lens.[9]

Previously, our group had proposed three kinds of nano-structured alignment surfaces.[10–12] They contained nano-sized alignment domains with both planar and vertical pretilt alignment properties. Several techniques had been investigated for forming these nano-sized domains, for example, by phase segregation during the drying of mixed fluids (Nanostructured of the first kind), dewetting (Nanostructured of the second kind) and nanoimprint lithography combined with plasma irradiation (Nanostructured of the third kind). These alignment surfaces were mainly designed for producing arbitrary pretilt and azimuth angles.

In this work, we demonstrate a new kind of nano-structured alignment surface which is designed to have bistable azimuthal alignment directions. This nano-alignment surface consists of two alignment layers stacked together, including a photoalignment polymer, which is similar to the Nanostructured of the second kind. In addition, like the Nanostructured of the third kind, it contains a nano-grooved structure. However, unlike the Nanostructured of the third kind; this nano-groove layer can be used to align liquid crystal molecules directly as the dimension of the groove is small. Here we show that the proposed bistable alignment surface can have two stable azimuthal alignment directions. The resultant azimuthal alignment directions are controlled by the azimuthal anchoring energies of both the nano-groove surface and the top photoalignment layer. The fabrication of this bistable alignment surface relies simply on nano-imprint technology. The sizes of the nano-groove are fixed and controllable. The alignment surface is robust, stable, reliable, reproducible and favorable for mass manufacturing. In other words; this nano-structured alignment surface can be used to fabricate a π/2 bistable twisted nematic (π/2-BTN) display.

The structure of the proposed bistable alignment surface is shown in Fig. 1. The bistable alignment surface consists of two layers stacked together. The bottom layer is a nano-sized groove surface which is drawn in red color. In addition, there is a photo-alignment polymer on top of the grooved surface and is indicated by blue color. λ is defined as the nano-groove's pitch. While a is defined as the depth of the nano-groove and in combination with the top alignment layer. The top alignment layer will both fill up the trough of the original groove and stack on the crest of the original groove. It should be noticed that for the top alignment layer, the filled up thickness might not be equal to the stacked up thickness because of different surface profile of the bottom groove layer.

The creation of the nano-groove surface relies on nano-imprint technology. As the required patterned is just some simple stripe patterns, nano-imprint lithography is more preferable than the normal photolithography. It is because the nano-imprinting is more reliable for the sub-wavelength scale and large area fabrication by roll to roll processing. A nano-imprinting mask can be applied for controlling the pitch and depth of the grooves. The nano-groove surface indeed can be fabricated by using any materials, for example, photoresist, polymer or oxide. It needs not to be a liquid crystal alignment material. As the alignment effect of the nano-groove to the liquid crystal molecules is induced by its physical groove

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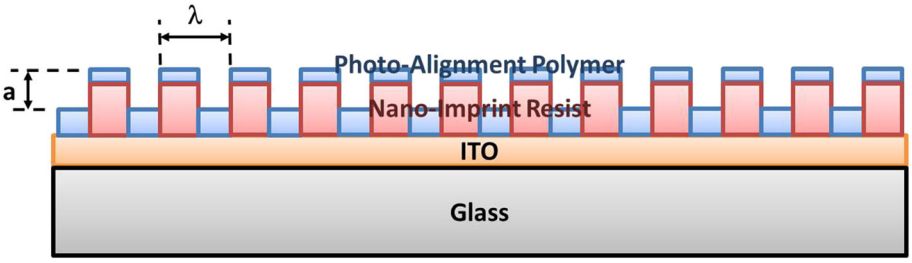

FIGURE 1 — An overview of the proposed bistable nano-alignment surface.

structure directly.[13,14] The nano-groove surface gives liquid crystal molecules a preferred azimuthal alignment direction along its groove direction. From the previous study,[13] the azimuthal anchoring energy of this nano-groove surface, W_g, can be calculated by Eq. (1):

$$Wg = \frac{2K\pi^3 a^2}{\lambda^3} \tag{1}$$

where K is the elastic constant of the liquid crystal, and a and λ are the depth and pitch of the groove surface respectively. Figure 2 plots the calculated azimuthal anchoring energy of the nano-groove surface versus different groove depths and pitches using Eq. (1). The anchoring energy is non-linear and can be varied in a large range from 1×10^{-2} J/m^2 to 1×10^{-7} J/m^2, depending on the groove depth and pitch.

A second alignment layer is further coated on top of the nano-groove surface. Photoalignment material is more preferable than conventional rubbed polyimide for the second alignment layer. As the rubbing process may damage the bottom grooved surface; although theoretically speaking it will work for any alignment materials. It should be noticed that after coating the second alignment layer, the azimuthal anchoring energy of the nano-groove surface will be reduced; as the grooves become shallower. The second alignment layer should produce an azimuthal alignment direction perpendicular to the nano-groove surface and with azimuthal anchoring energy, W_a. In addition, this layer can be fabricated either completely cover the groove surface (continuous) or forming domains on top of the grooved surface (discontinuous) by controlling the dewetting condition, and the concentration of the second alignment material dissolved in a solvent.[15] Such effect can be applied to influence the azimuthal anchoring energy of the second alignment layer. Hence, the resultant azimuthal anchoring energy of the second alignment layer, W_a, will be proportional to the concentration of the second alignment material and also the coverage of the nano-groove surface. As the top layer is spin-coated on a grooved surface, the thickness of the top layer is indeed not uniform. Intuitively, the solution will tend to fill up the trough of the groove more than stacking up on the crest of the groove if the bottom surface is a wettable surface.[16] Such effect will result in different thickness of the second alignment layer at the peak and at the trough. Hence, as the thickness of the second alignment layer increases, the height of the grooved structure indeed decreases.

Bistability of the alignment surface occurs if the azimuthal anchoring energies of the nano-groove and top alignment layer are the same and the directions are perpendicular to each other. The alignment directions and anchoring energies of the two alignment layers together with the resultant two stable alignment directions are drawn in Fig. 3.

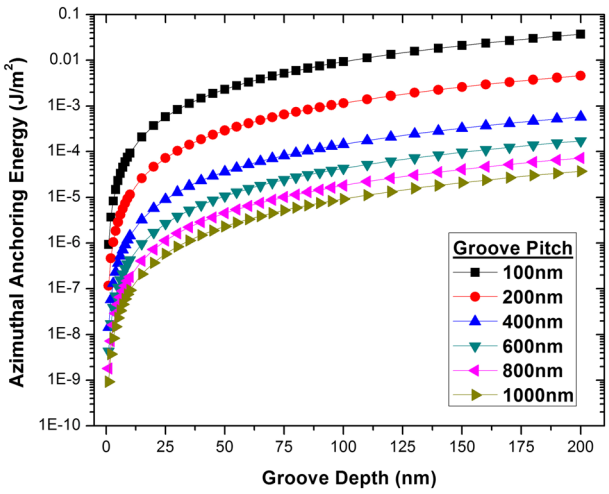

FIGURE 2 — Calculated azimuthal anchoring energy versus different groove depths and pitches.

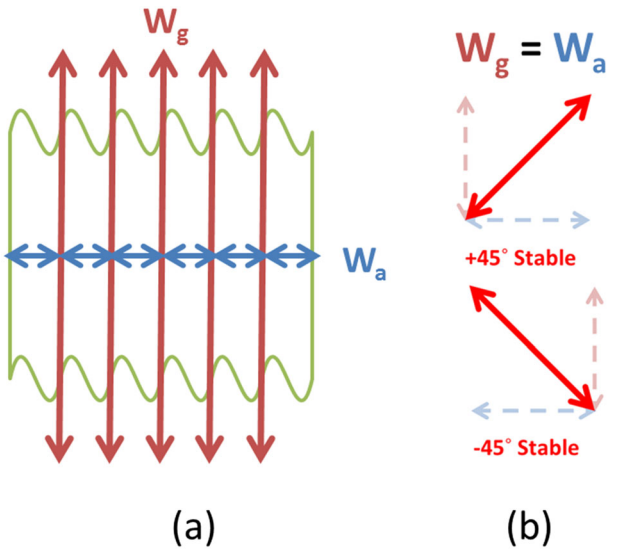

FIGURE 3 — (a) The alignment directions of the nano-groove surface and the top photoalignment layer. (b) The resultant bistable azimuthal alignment directions.

Figure 4 plots the simulated resultant azimuthal direction, ϕ_r, of the bistable alignment surface versus different thickness of the second alignment layer. For simplicity, the thickness of the second alignment layer was considered to be the mean thickness over the crest and trough area. The azimuthal anchoring energy, W_a, of the second alignment layer was assumed to be 5×10^{-4} J/m^2 when its thickness was larger than 10 nm. The alignment directions of the nano-groove and second alignment layer were set at $\phi_g = 90°$ and $\phi_a = 0°$ respectively. The area coverage ratio of the second alignment layer was 100%, i.e. no dewetting occurs. The pretilt angles were zero for both layers. In addition to the thickness of the second alignment layer, the pitch and depth of the nano-groove were also varied. When the second alignment layer is thin, the nano-groove dominates the alignment direction; as W_g is much larger than W_a. Moreover, if the second alignment layer is extremely thin, i.e. <10 nm, W_a further depends on its own thickness. B the bottom grooved surface is a wettable surface; the second alignment layer will fill up the groove after spin-coating, i.e. Wenzel's state.[17] When the thickness of the second alignment layer increases, the groove depth decreases; hence W_g decreases accordingly. ϕ_r is indeed a vector summation of the two alignment layers. Eventually when W_g equals to W_a, the resultant azimuthal alignment direction, ϕ_r, is achieved at 45° and bistability alignment direction occurs.[18] From the simulation results, it can be seen that in order to maximize the processing window; it is necessary to choose a right combination of nano-groove's pitch, λ, and depth, a. The reason is because of the non-linearity of Eq. (1).

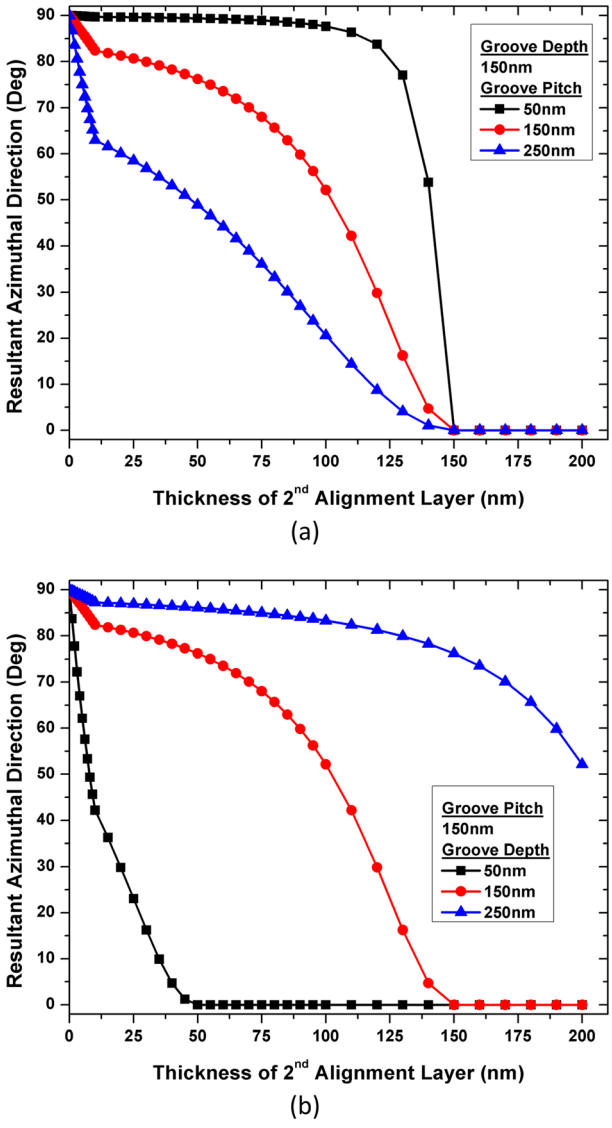

FIGURE 4 — Simulated resultant azimuthal alignment direction versus different second alignment thickness with different (a) groove pitch and (b) groove depth.

In order to verify the alignment property of the nano-sized groove surface, a grooved surface was fabricated. The following describes the details of the experiment procedures. First, a commercial nano-imprint resist AMONIL MMS4 provided by AMO GmbH, Germany was spin coated on a well-cleaned indium tin oxide (ITO) glass substrate. The imprint resist is a hydrophilic material with contact angle

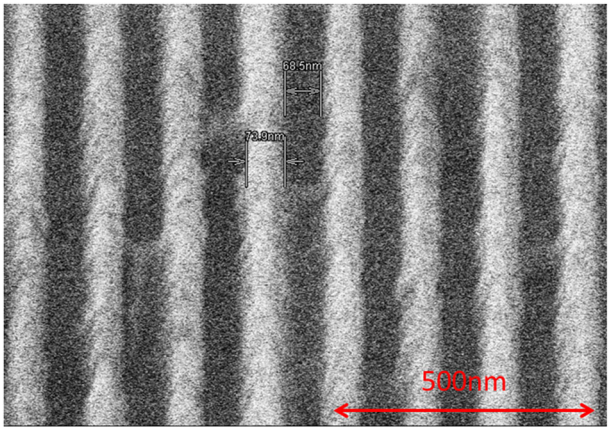

FIGURE 5 — Scanning electron microscope (SEM) picture of the nano-groove surface.

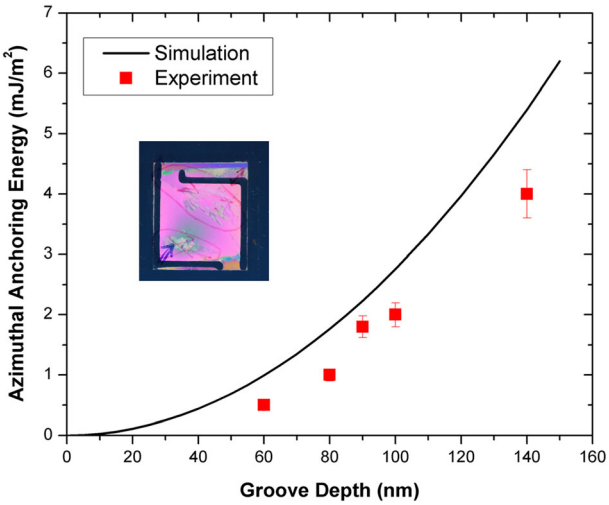

FIGURE 6 — Measured azimuthal anchoring energy of the nano-groove surface.

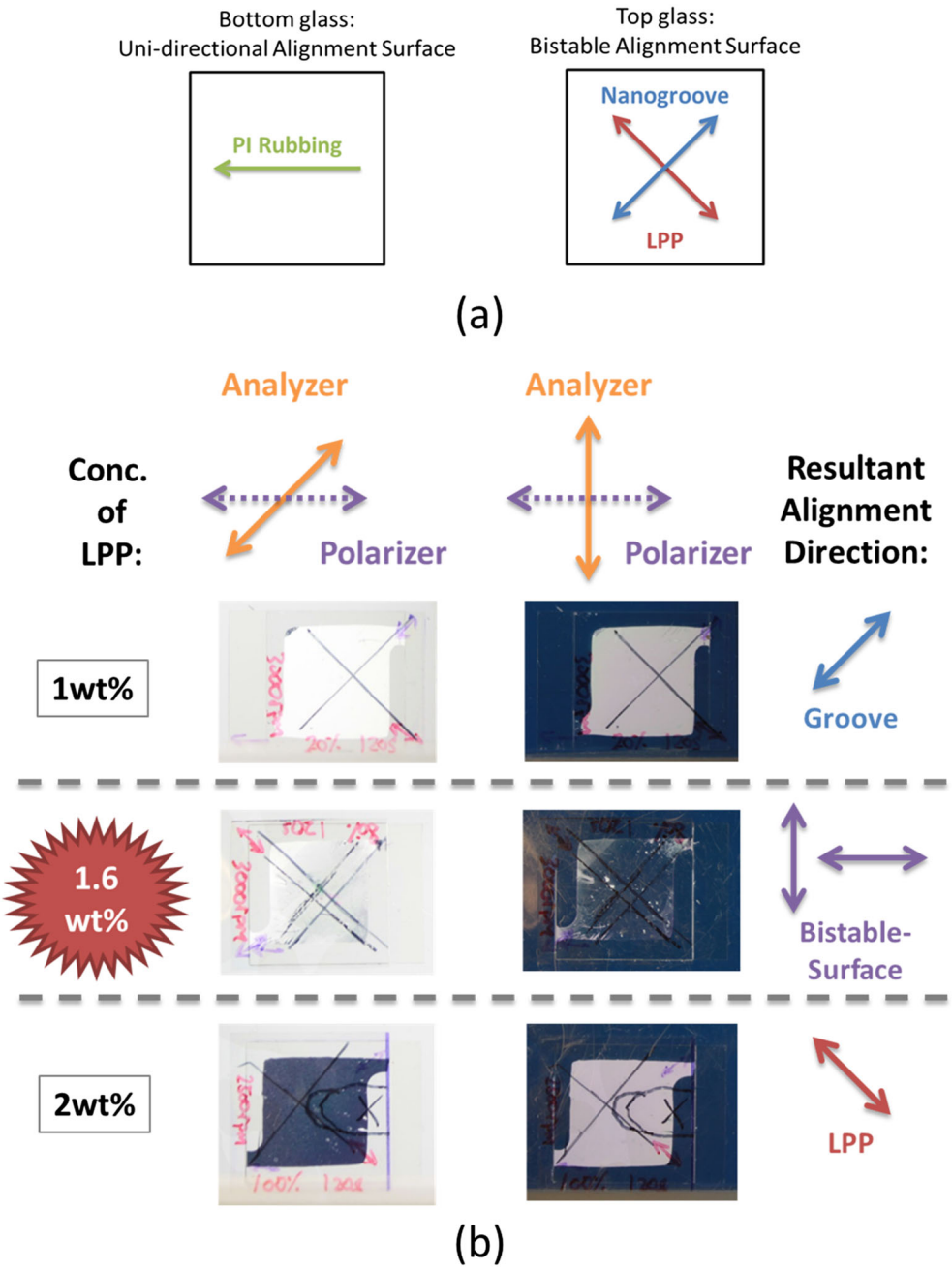

FIGURE 7 — (a) Top and bottom alignment directions of the test cells. (b) Fabricated test cells with different LPP concentrations placed in between crossed polarizers.

measured to be 60°.[19] Nano-imprinting was then performed. A 150-nm pitch and 130-nm height flexible polyurethane acrylate (PUA) nano-imprint grating mold which is fabricated by electron-beam (e-beam) lithography was brought into intimate contact with the substrate. By applying pressure, the features on the mold were transferred to the imprint resist. The whole setup including the substrate and the mold were then exposed by unpolarized ultraviolet (UV) light through the backside of the mold in order to cure and harden the imprint resist. The groove depth could be adjusted by putting the substrate into a reactive ion etching (RIE) machine for oxygen (O_2) reactive ion etching. As the etching time increases, the groove depth becomes shallower. Azimuthal anchoring energy was then measured by the torque balance method.[20–23] Figure 5 shows the scanning electron microscope (SEM) picture of the nano-groove surface. From the SEM picture, the width of the peak and trough is about 75 nm and 70 nm respectively. And the height of the groove is about 150 nm after the nano-imprint lithography without any RIE etching. Figure 6 plots the measured azimuthal anchoring energy versus different groove depths. The azimuthal anchoring energy increased from 0.5 mJ/m^2 to 4 mJ/m^2 as the

groove depth increased from 60 nm to 150 nm. The difference between the measured and the calculated anchoring energies may because of the imperfect grating dimension. Nevertheless, the azimuthal anchoring energy is still high and can be used to align liquid crystal directly. A 5 µm electrically controlled birefringence (ECB) cell filled with liquid crystal MLC-6080 ($\Delta n = 0.2024$) from Merck Corporation, Germany, is successfully fabricated as shown in the sub-picture.

For the bistable surface, a second alignment layer was further deposited on top of the nano-groove surface. A commercial linearly photo-polymerizable photoalignment polymer (LPP), ROP-103, provided by Rolic Technologies Limited, Switzerland, was used to be the second alignment layer. The polar and azimuthal energies were measured to be 1 mJ/m^2 and 0.5 mJ/m^2 respectively. The use of photoalignment polymer can eliminate mechanical rubbing, hence prevent scratching of the nano-groove surface. The polymer was diluted with the solvent Cyclohexanone to a variety of solid concentrations. As the concentration of the LPP increased, the thickness of this layer also increased accordingly. The following describes the details of the experiment procedures. After fabricating the nano-groove surface, the substrate was spin-coated with the LPP solution. The substrate was then put on a hot plate for soft baking. At last, the substrate was exposed by a linearly polarized UV (LPUV) light at wavelength of 280–340 nm at normal incident angle with the polarization axis perpendicular to the groove direction. The azimuthal orientation direction of the LPP was defined parallel to the plane of LPUV polarization. As a result, the second azimuthal alignment direction could be obtained. In order to prove the bistability of the surface, several test cells with different solid concentrations of LPP were fabricated. The cells were assembly with one conventional uni-directional alignment surface produced by rubbed polyimide surface and one bistable alignment surface. Figure 7 shows the fabricated cells placed in between a pair of polarizers. Clearly, when the concentration of LPP equaled to 1.6 wt%, the resultant azimuthal alignment direction was neither the groove direction nor the LPP polymerized direction. The depth, *a*, of the stacked groove structure, i.e. bottom nano-groove combined with different weighted concentration of LPP had been measured by using section analysis. Figure 8 plots the measured depth results. Clearly the groove structure was diminishing as the concentration of LPP increased. Finally at 2 wt% of LPP, the top layer was nearly covered the entire groove and became a flat surface. Such observation agrees with our previous prediction.

The bistable nano-structured alignment surface can be applied to fabricate a π/2 bistable twisted nematic (π/2-BTN) display. The two stable states of the π/2-BTN display are untwisted (0°) and twisted (90°) states. Such bistable display has many advantages, e.g. high transmittance, excellent contrast, no color dispersion, good viewing angle, cell gap independent and fast response time. When placed in between 0° and 90° crossed polarizers (e-mode), the untwisted state is

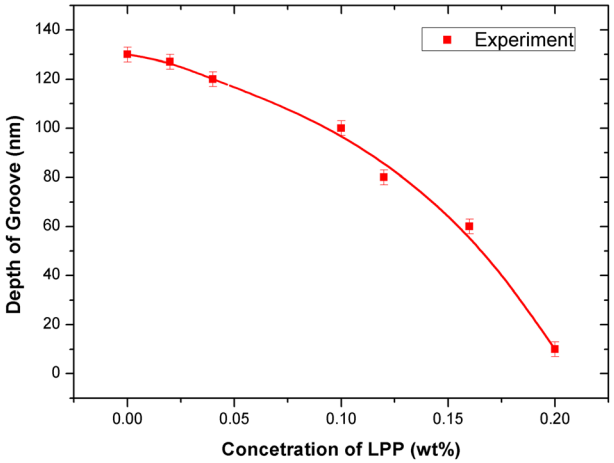

FIGURE 8 — Measured groove depth of the stacked groove structure versus different concentration of LPP.

the dark state, while the twisted state is the bright state. The optical performance is the same as conventional normally white twisted nematic (NW-TN) display and can be easily optimized. Figure 9 plots the transmittance of a π/2-BTN display and π-BTN display as a comparison. Another benefit of the π/2-BTN display over the traditional π-BTN display is the cell gap independent, i.e. d/p ratio, because the bistability is achieved by the alignment surface inherently. A single pixel π/2-BTN demo prototype was successfully fabricated. Figure 10 shows the photo of the sample placed under a pair of crossed polarizers. The cell was filled with liquid crystal MLC-6204-000 ($\Delta n = 0.1478$) from Merck Corporation, Germany. The cell gap was 6 µm. One of the substrates was coated with ordinary rubbed polyimide with pretilt angle 2°. The pretilt angle was measured by using the crystal rotation method.[24] The other substrate had a bistable alignment surface. Switching was achieved by using two orthogonal in-plane electrodes which can provide different horizontal electric field direction. The schematic of this electrode is drawn

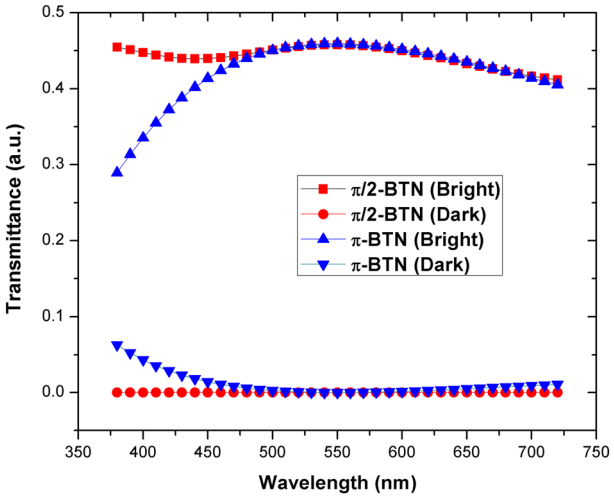

FIGURE 9 — Transmittance spectrum of the π/2-BTN and π-BTN displays.

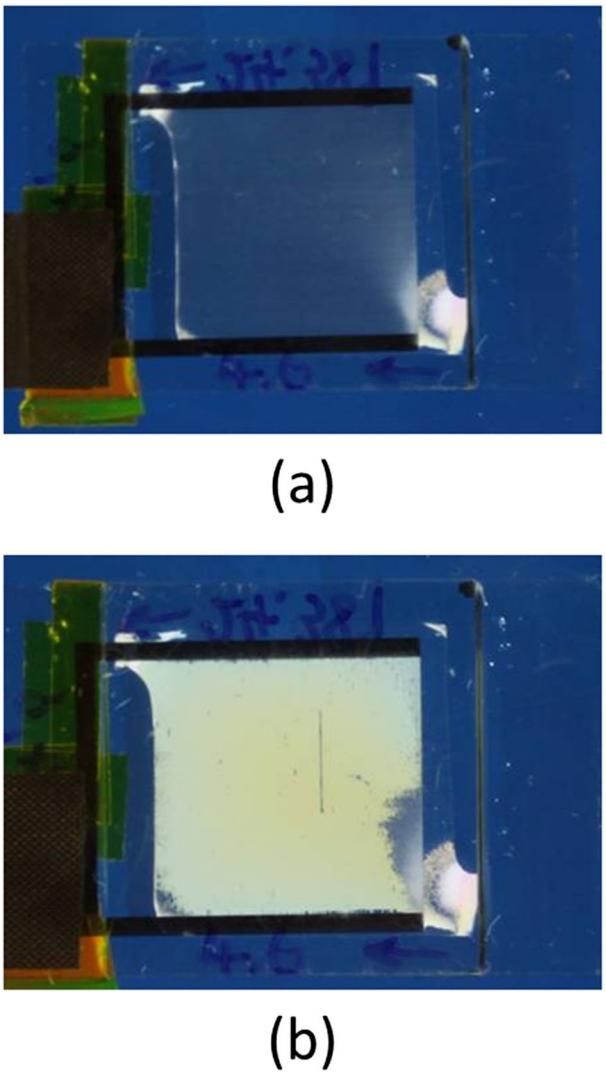

FIGURE 10 — Photo of the fabricated π/2-BTN sample cell placed in between crossed polarizers with (a) dark state and (b) bright state.

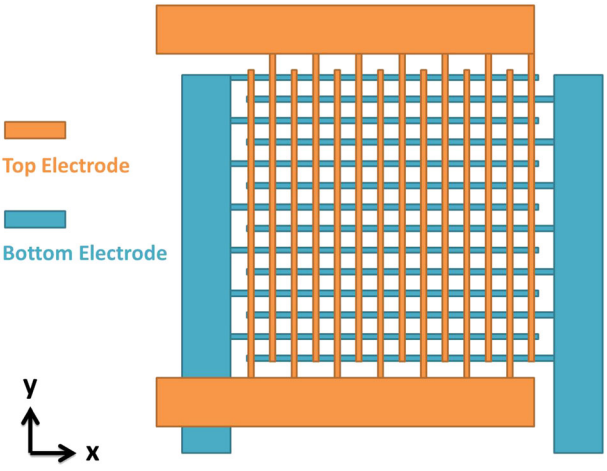

FIGURE 11 — Schematic drawing of the stacked in-plane electrodes structure.

in Fig. 11. The bottom electrode was first patterned. Then a 100-nm-thick SiO_2 was deposited as an insulator layer. After patterning the top aluminum electrode, the un-overlapped SiO_2 area was etched by using top electrode as a shadow mask which can give larger electric field strength. Aluminum top electrode was used to reduce the resistance although it would reduce the transmittance of the bright state. The width of the electrode is 4 μm and with 10-μm pitch. The driving voltage is 15 V. The π/2-BTN showed bistability of the two states with lifetime observed to be more than 1 month.

In summary, we have demonstrated a bistable nano-structured alignment surface. The surface has two stable azimuthal alignment directions. The surface consists of a nano-sized groove and a photo-alignable polymer stacked together. Bistability occurs when these two layers have the same azimuthal anchoring energies but in perpendicular alignment directions. Such bistable alignment surface can be used to fabricate π/2-BTN display which has the advantage of high contrast ratio, less color dispersion and cell gap independent.

Acknowledgments

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References

1 L. Komitov *et al.*, "Controllable alignment of nematics by nanostructured polymeric layers," *Liquid Crystals* **36**, 747–753 (2009).
2 X. Lu *et al.*, "Substrate patterning for liquid crystal alignment by optical interference," *Appl. Phys. Lett.* **88**, 243508 (2006).
3 K. Zhang *et al.*, "Pretilt study of double-layer alignment film (DLAF)," *Liquid Crystals* **35**, 1191 (2008).
4 G. P. Sinha *et al.*, "Large, continuously controllable nematic pretilt from vertical orientation," *Appl. Phys. Lett.* **79**, 2543 (2001).
5 F. S. Yeung *et al.*, "Variable liquid crystal pretilt angles by nanostructured surfaces," *Appl. Phys. Lett.* **88**, 051910 (2006).
6 J. T. K. Wan *et al.*, "Liquid crystal pretilt control by inhomogeneous surfaces," *Phys. Rev. E* **72**, 021711 (2005).
7 Y. W. Li and H. S. Kwok, "Bistable twisted-bend and twisted-nematic liquid crystal display," *Appl. Phys. Lett.*, **95**, 181107 (2009).
8 F. S. Y. Yeung and H. S. Kwok, "Fast-response no-bias-bend liquid crystal displays using nanostructured surfaces," *Appl. Phys. Lett.*, **88**, 063505 (2006).
9 M. C. Tseng *et al.*, "Tunable lens by spatially varying liquid crystal pretilt angles," *J. Appl. Phys.*, **109**, 083109 (2011).
10 C. Y. Lee *et al.*, "Nano-structured alignment layer for liquid crystals," *Journal of the SID* **21**, 407 (2014).
11 H. S. Kwok and F. S. Y. Yeung, "Nano-structured liquid-crystal alignment layers," *Journal of the SID* **16**, 911 (2012).
12 C. Y. Lee *et al.*, "Variable liquid crystal pretilt and azimuth angle using stacked alignment layers," *SID Sym. Dig. Of Tech. Papers* **40**, 1619 (2009).
13 X. Lu *et al.*, "Alignment mechanism of a nematic liquid crystal on a pre-rubbed polyimide film with laser-induced periodic surface structure," *Liquid Crystals* **30**, 985 (2003).
14 D. W. Berreman, "Solid surface shape and the alignment of an adjacent nematic liquid crystal," *Phys. Rev. Lett.* **28**, 1683 (1972).
15 C. Y. Lee *et al.*, "Discontinuous alignment thin-film formation by self-organized dewetting," *SID Sym. Dig. Of Tech. Papers* **41**, 591 (2010).
16 R. Seemann *et al.*, "Patterning of polymers: precise channel stamping by optimizing wetting properties," *New J. of Phys.* **6**, 111 (2004).

17 X. Feng and L. Jiang, "Design and creation of superwetting/antiwetting surfaces," *Adv. Mater.*, **18**, 3063 (2006).
18 O. K. C. Tsui *et al.*, "First-order liquid crystal orientation transition on inhomogeneous substrates," *Phys. Rev. E* **69**, 021704 (2004).
19 J. Ryu *et al.*, "A study of contact angles according to the resist thickness and imprint time effects during NIL," *Microelectronic Engineering* **98**, 210 (2012).
20 Y. Zhou *et al.*, "Generalized relation theory of torque balance method for azimuthal anchoring measurements," *Jpn. J. Appl. Phys.* **38**, 4857 (1999).
21 M. Jiang *et al.*, "Method of studying surface torsional anchoring of nematic liquid crystal," *Jpn. J. Appl. Phys.* **33**, L1242 (1994).
22 Y. Imura *et al.*, "A new method for measuring the azimuthal anchoring energy of a nematic liquid crystal," *Jpn. J. Appl. Phys.* **33**, L434 (1994).
23 V. P. Vorflusev *et al.*, "Azimuth anchoring energy in photoinduced anisotropic films," *Jpn. J. Appl. Phys.* **34**, L1137 (1995).
24 K. Shirota *et al.*, "Modified crystal rotation method for measuring high pretilt angle in liquid crystal cells," *Jap. J. Appl. Phys.* **34**, 9A, 4905–4908 (1995).

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