Control of liquid crystal pretilt angle by anchoring competition of the stacked alignment layers

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We proposed a method to control the pretilt angle of liquid crystals by stacking of a vertical alignment layer on a planar alignment layer. The pretilt angle can be controlled over the full range (0°–90°) depending on the thickness of the vertical alignment layer. We also proposed a numerical model to describe the physical mechanism based on the anchoring competition between liquid crystal, planar, and vertical polyimide alignment layers. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3068003]

The preparation of highly oriented liquid crystals (LCs) is of great importance for the basic understanding of interfacial phenomena and for the fabrication of electro-optical devices including LC displays (LCDs). The operation of most of these devices is based on either planar or vertical alignment of the LC molecules using alignment materials such as polyimides (PIs), photopolymers, surfactants, silicon oxide, and so on.[1] However, there is high demand for the tilted alignment of LCs between planar and vertical. In the optical configuration of LCDs, the pretilt angle is one of the most important parameters because it strongly influences the electro-optics properties of various LCD modes. Recently, various methods have been developed to control the pretilt angle over the whole range (0°–90°), such as mixing vertical and planar PIs,[2,3] microtextured formation using atomic force microscope,[4,5] and ion beam exposure of silicon carbide films.[6] Among these methods, the mixture of planar and vertical alignment layers has attracted much attention because it produced a thermally stable pretilt angle, which is a critical factor in the mass production of LCDs. More recently, Kim *et al.*[7] reported that the pretilt angle could be controlled using a double layer with different rubbing strengths. In these two cases, the pretilt angle is controlled by the competition of planar and vertical anchoring in the same plane due to nanostructured or scratched surfaces. Although the control of the pretilt angle from 0° to 90° was achieved, these methods suffered reproducibility problems because the formation of such microdomains depends on various parameters, such as temperature, uniformity of the mixture, or rubbing strength.

In this article, we propose a method to control the pretilt angle of LCs by stacking of a vertical alignment layer on a planar alignment layer. The pretilt angle is controlled continuously from 0° to 90°, depending on the thickness of the vertical alignment layer. We also propose a numerical model to describe the physical mechanism based on the competition of surface anchoring energy in the vertical direction.

To produce an intermediate pretilt angle, we stacked two alignment layers that produce the planar and vertical LC alignments, respectively, as shown in Fig. 1. Although the upper alignment layer has a direct influence on the LC, the alignment capability induced from the lower alignment layer is screened partially or entirely depending on the thickness of the upper alignment layer. Thus, if we controlled the thickness of the upper alignment layer to produce competition in the LC alignment, then the pretilt angle could be controlled continuously. In the experiment, we used a planar PI alignment layer (SE7492 from Nissan Chem.) with a 5° pretilt angle and a vertical PI alignment layer (AL60101 from JSR) with an 89° pretilt angle for the lower and upper layers, respectively. The planar alignment layer was obtained by spin coating and prebaking the sample at 80 °C for 10 min, followed by curing for imidization at 210 °C for 2 h. For tuning the thickness of the vertical alignment layer, we diluted the PI materials with a solvent consisting of a mixture of n-methyl-pyrrolidone, buthyrolactone, and butoxyethanol according to each thickness condition. The mixture of the vertical alignment material and the solvents was spin coated on the unrubbed planar alignment layer and prebaked at 80 °C for 10 min and cured at 180 °C for 1 h. Then, the surface was rubbed using a rubbing machine with antiparallel direction and the cell was filled with LC (ZKC-5085XX, Chisso). The thickness of the vertical alignment layer was measured using a spectroscopic ellipsometer (Unisel-ER, Horiba).[8] Pretilt angles were measured in 13 μm thick cells using the polarizer rotation method.[9]

Figure 2 shows the pretilt angle of the LC as a function of the thickness of the vertical alignment layer. The pretilt angles were controlled continuously in the range of 5°–89°. These results are reproducible and reliable within error

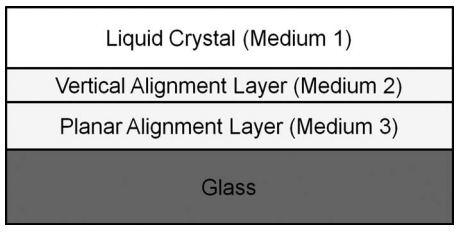

FIG. 1. The schematic diagram of the proposed stacked alignment layer system.

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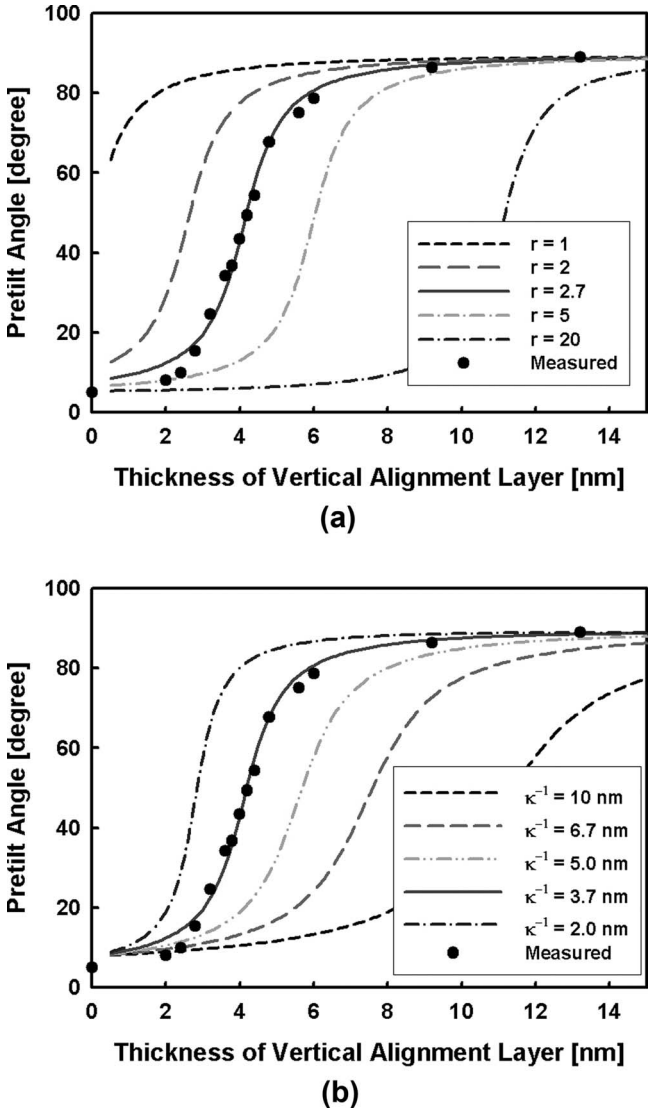

FIG. 2. Pretilt angles as a function of the thickness of the vertical alignment layer. The dots are experimental results and the solid lines are calculated as varying with (a) r and (b) κ^{-1}.

ranges. The solid lines in Fig. 2 are the results of calculations using a numerical model with different values of r and κ^{-1}, which is the ratio of polarizability and the screening length, respectively, discussed below.

Since we used a conventional spin coating method, this method can easily be applied to conventional mass production of LCDs. The other important factor in the fabrication of LCDs is the thermal stability of the pretilt angle. Figure 3(a) shows the change in pretilt angle of 12°, 47°, and 82° as a function of annealing time at 100 °C. The pretilt angles maintained almost the same value throughout the test. The inset boxes in Fig. 3(a) are microscopic textures at each testing condition, which also maintained a uniform appearance over the course of the test. Based on these results, this technique should be very reliable for the mass production of LCDs. Figure 3(b) shows the pretilt angles for different number of rubbings (i.e., different surface roughnesses). The pretilt angles maintained almost the same value. This result suggests that the pretilt angle in our sample is not determined by the surface morphology as in the results of Kim *et al.*[7]

The difference in the surface properties with changes in the thickness of the upper vertical alignment layer can be

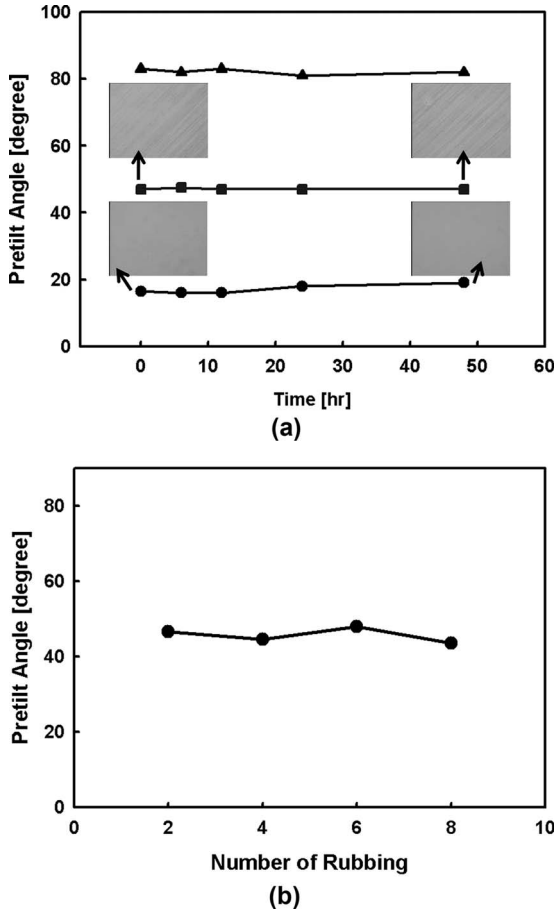

FIG. 3. (a) Stability of the pretilt angles as a function of heating times at 100 °C for cells that have the pretilt angles of 12°, 47°, and 82°, respectively. The inset boxes are microscopic textures at each testing condition. (b) Pretilt angles for different cycles of rubbing.

confirmed by the measurement of contact angles on each sample, as shown in Fig. 4. Since the vertical alignment layer is hydrophobic relative to the planar alignment layer, the contact angle increased with increasing thickness of the vertical alignment layer. Thus, the surface anchoring properties gradually changed with different thicknesses of the vertical alignment layer by the screening of polar anchoring energy from the planar alignment layer.

Now we consider the physical mechanism for why the control of the pretilt angle is based on the thickness of the vertical alignment layer. Our system consists of three layers: a nematic LC (medium 1), a vertical PI with thickness l

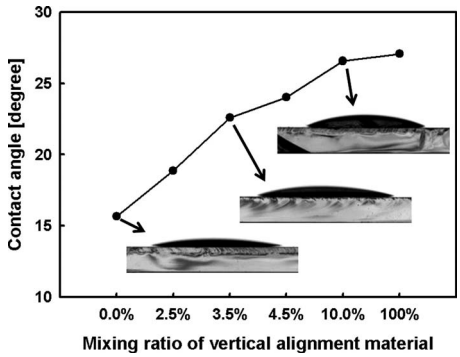

FIG. 4. Contact angles for different thicknesses of upper vertical alignment layer.

(medium 2), and a planar PI (medium 3) on a glass substrate, as shown in Fig. 1. The total free energy per unit surface area for a uniform nematic orientation is

$$f = f_{12} + f_{13} + f_{23}, \tag{1}$$

where f_{ij} is the energy of interactions between medium i and medium j. In Eq. (1), we can neglect the term f_{23} because this interaction is independent of the orientation of LC molecules. Further, the angular dependencies of each energy can be described by the Rapini–Papoular form as

$$f_{ij} = \tfrac{1}{2}A_{ij}\sin^2(\varphi_i - \varphi_j), \tag{2}$$

where A_{ij} is related to the polarizability of LC molecules, φ_i is the average angle of LC molecules, and φ_j is the easy axis of medium j. In Eq. (2), we can assume that f_{13} decays exponentially because the anchoring energy is screened by medium 2.[10] Therefore, f_{13} is written as follows:

$$f_{13} = \tfrac{1}{2}A_{13}e^{-\kappa l}\sin^2(\varphi_1 - \varphi_3), \tag{3}$$

where κ is a characteristic decay length, known as the Debye screening. Since f_{12} is not screened, the total free energy is given by

$$f = \tfrac{1}{2}w_{13}\sin^2(\varphi_1 - \varphi_3) + \tfrac{1}{2}A_{12}\sin^2(\varphi_1 - \varphi_2), \tag{4}$$

where $w_{13}(l) = A_{13}e^{-\kappa l}$. A pretilt angle, φ_1, obtained by minimization of the total surface free energy f with respect to φ_1 is given by

$$\tan(2\varphi_1) = \frac{w_{13}(l)\sin(2\varphi_3) + A_{12}\sin(2\varphi_2)}{w_{13}(l)\cos(2\varphi_3) + A_{12}\cos(2\varphi_2)} = \frac{re^{-\kappa l}\sin(2\varphi_3) + \sin(2\varphi_2)}{re^{-\kappa l}\cos(2\varphi_3) + \cos(2\varphi_2)}, \tag{5}$$

which shows that the pretilt angle φ_1 depends on the thickness l of the vertical PI layer when the values $\varphi_3 \neq 0$ at $\varphi_2 = \pi/2$ (or $\varphi_3 \neq \pi/2$ at $\varphi_2 = 0$). For the special case in which $\varphi_3 = 0$ and $\varphi_2 = \pi/2$, Eq. (5) gives $\tan(2\varphi_1) = 0$, i.e., $\varphi_1 = 0$ or $\pi/2$. In Eq. (5), if the interaction with the planar PI layer is perfectly screened (i.e., $w_{13} \to 0$), then the pretilt angle of the LC is solely determined by the vertical PI layer ($\varphi_1 \to \varphi_2$). However if l is sufficiently small, then anchoring competition occurs and the pretilt angle can be controlled continuously by tuning the thickness of the vertical alignment layer.

The solid lines in Fig. 2 are the result of calculations based on Eq. (5). The fitted value of κ^{-1} and the ratio of $r = A_{13}/A_{12}$ were 3.7 nm and 2.7, respectively. Experimentally, the ratio A_{13}/A_{12} was measured from the surface polar anchoring energy of the vertical and planar alignment layers using the high voltage method.[11] The measured surface polar anchoring energies of the vertical and planar alignment layers were 3.2×10^{-4} and 1.1×10^{-4} J m^{-2}, respectively. As a result, the measured value of $r = A_{13}/A_{12}$ was 2.9, which agrees well with the calculated result. In Fig. 2 with increasing values of r, the plots were shifted to the right. It means that the tuning range of the thickness of the vertical alignment layer can be controlled by the materials with different surface polar anchoring energies. Figure 2(b) shows the effect of the variation in the value of κ^{-1}, called the screening length, which depends on material properties such as dielectricity, conductivity, and ion contamination. If we select alignment materials that have a large value of κ^{-1}, we can obtain a wide process window.

In summary, we proposed a method that can quantitatively control intermediate pretilt angles via an anchoring competition between planar and vertical PI alignment layers. The anchoring competition generated by the vertical alignment layer that screened the anchoring energy of the underlying planar alignment layer was found to depend on the thickness of the layer. Since the proposed technique does not modify the PI materials and manufacturing processes, we can apply conventional alignment processes. Moreover, thermal stability is also as good as conventional alignment materials over the whole range of pretilt angles.

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