Anchoring Competition on Nanosurface Boundaries with Conflicting Mixed Nematic Anchoring Properties

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We propose a technique for continuously controlling the full range of pretilt angles with a high process margin. The proposed method is characterized by tuning the thickness of a heterogeneous polyimide layer that consists of homeotropic and planar polyimides. The thickness of the mixture can be controlled by varying the concentration of the solvent. The liquid crystal (LC) pretilt generated at the very thin mixture film is insensitive to some incorrect mixing ratio, since the segregation of the depth direction of the mixture including the van der Waals effect in interactions with LCs decreases ultimately. Consequently, we can obtain continuous LC pretilt angles with a high process margin by controlling mixing ratio in a very thin heterogeneous polyimide film. Furthermore, it is possible to achieve excellent reliability, uniformity, and productivity using this technique. A simple mathematical model based on van der Waals interaction provides a good description of the experimental results.
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1. Introduction

Many scientists are interested in the interface between a polymer surface and a liquid crystal, particularly in polar anchoring at the polymer-nematic boundary, the knowledge of which holds scientific and practical values.[1–10] In a nematic liquid crystal (LC) cell, the pretilt angle is one of the most important factors affecting the electrooptic characteristic of liquid crystal displays (LCD) and is thought to play a crucial role in advancing various LC device applications. Therefore, various approaches[11–20] to controlling, over a wide range, the pretilt of LCs have been attempted to advance LC applications. However, a method of producing a stable pretilt remains elusive.

Aligned hydrophilic surfaces lead to a homogeneous LC alignment. This reduces the elastic strain energy of the LC, while the hydrophobic surface drives the homeotropic LC alignment. As our first approach to controlling LC pretilt, if LCs are separated completely from the surface (hydrophilic material) by the hydrophobic material, as shown in Fig. 1(a), the anchoring state of the LC is determined by the thickness of the hydrophobic material. If LCs are separated gradually from the surface by some hydrophobic materials, the surface free energy will decrease and then a polar orientation transition may be induced continuously to lower their total free energy. This approach, using inhomogeneous surfaces for LC alignment, may give rise to another anchoring property. As such, the polar anchoring of the LC can be controlled using a distinct mixture showing a largely different surface activity. Since the pretilt angle of LC is deeply related to anchoring, the pretilt angle may be controlled successfully by this approach.

In general, if the hydrophobic layer is air or vacuum, the attractive pair potential between a LC molecule and a molecule from the surface is of the form $f(h) = -C/h^n$, where C is the London dispersion force coefficient.[21] Then, with the further assumption of additivity, the net interaction energy between an LC molecule and the planar surface will be the sum of its interactions with all the molecules in the body with a hydrophilic property. For the van der Waals potential ($n = 6$), the net interaction energy for an LC
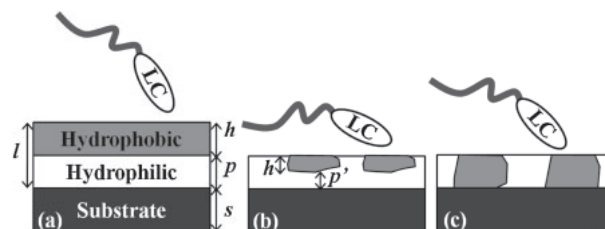

Fig. 1. Schematic diagram of LC formation depending on surface property; (a) when LCs are separated completely from the hydrophilic material by the hydrophobic material, (b) when LCs are separated partially from the hydrophilic material by the hydrophobic material, and (c) when LCs interact directly with mixture mixed completely.

molecule at a distance h from the surface will be $F(h) = -W/h^3$, where W is the van der Waals constant related to the polarizability of LC molecules. On the other hand, if the hydrophobic material is a liquid or solid, the net interaction energy is of the form $F(h) = -We^{-kh}$, which takes into account the screen effect, where k is the characteristic decay length, known as the Debye screening.[21] In general, the van der Waals force, $k^{-1} < 5$ nm.[21] This indicates that the interaction energy is changed abruptly by even small changes in the thickness of the sandwiched matter. As such, it is not easy to produce a reliable LC pretilt in the LCD fabrication.

On the other hand, if LCs are separated randomly and partially by hydrophobic materials, as shown in Fig. 1(b), the state of the LCs will be determined dominantly by the area ratio of the distinct mixture exposed to the exterior and the thickness of the hydrophobic medium. Here, the diameter of the local area of each matter should not be more than 1 μm to prevent the creation of independent LC domains.[14] In this case, the anchoring variation is relatively insensitive because the anchoring effect of the hydrophilic medium in the region covered by the hydrophobic medium is insignificant.

In an ideal case, if mixtures are mixed completely as shown in Fig. 1(c), the state of the LCs will be determined only by the area ratio of the distinct mixture. The anchoring variation in this case is not sensitive to the van der Waals force, which depends on the third power of the distance. Thus, this method is suitable for producing a reliable LC

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pretilt in the LCD fabrication. On the basis of these concepts, we demonstrate a full-range pretilt control technique using two mixed polyimides (PIs) with largely different surface properties. The key idea in the proposed technique is to establish a high margin process, where only a very thin film of the mixture is required to prevent the segregation of the mixture in the depth direction. This phase separation in the depth direction is always generated by the difference between the free energies of the two media.

2. Theoretical Model

Here, we want to establish a very simple mathematical model that can describe the schematic shown in Fig. 1. Firstly, we assume that the inhomogeneous domain on the mixture surface is very small, i.e., less than the coherent length of the LC. Therefore, the contribution of the two types of domain in the interaction between the LC and each domain can be regarded as only the surface area ratio, which determines the average pretilt of the LC. Thus, the total surface free energy density of this system at the Legendre polynomial[22,23] can be given simply by

$$F_t = \frac{1}{2}aA_h + \frac{1}{2}bA_p + \frac{1}{2}aA_p'e^{-kh} + \frac{1}{2}A_se^{-kl}, \quad (1)$$

where

$$A_h = \sum_{n=1}^{i} W_{hn}(1 - e^{-kh})\sin^n(\theta - \theta_h),$$

$$A_p = \sum_{n=1}^{i} W_{pn}(1 - e^{-kp})\sin^n(\theta - \theta_p),$$

$$A_p' = \sum_{n=1}^{i} W_{pn}(1 - e^{-kp'})\sin^n(\theta - \theta_p),$$

$$A_s = \sum_{n=1}^{i} W_{sn}(1 - e^{-ks})\sin^n(\theta - \theta_s).$$

The first term of eq. (1) describes the direct interaction between LCs and homeotropic PI with area a, the second term means the direct interaction between LCs and planar PI with area b, the third term indicates the interaction between LCs and planar PI with area a screened by homeotropic PI, and the last term shows the interaction between LCs and the glass substrate. Here, θ is the average pretilt of the LCs and θ_h, θ_p, and θ_s are the easy axes of the LCs driven at the direct contact of LCs and the homeotropic PI, LCs and the planar PI, and LCs and the glass substrate, respectively. As a and b are the relative surface area ratios of the homeotropic PI and planar PI, respectively, it is clear that $a + b = 1$. h and l are the thicknesses of the homeotropic PI and mixture, respectively. p and p' are the thicknesses of the planar PI. W_{hn}, W_{pn}, and W_{sn} are the polar anchoring energies, at infinite thickness, of the homeotropic PI, planar PI, and glass substrate, respectively. We assumed that the screening effects k of the two media are the same. The easy direction of LCs, θ, on this frustrated surface should satisfy

$$\frac{dF_t}{d\theta} = 0. \quad (2)$$

In a phase separation region like that in Fig. 1(a), the second term on the right-hand side of eq. (1) is eliminated since $a = 1$ or $b = 0$ and then the pretilt θ is the function of only h.

Here, for a large thickness ($h > 10$ nm), the third and fourth terms on the right-hand side of eq. (1) are also negligible as they are nearly totally screened, therefore, $\theta \approx \theta_h$. In a perfectly mixing region like that in Fig. 1(c), for a large thickness of the mixture ($l > 10$ nm), the third and fourth terms are negligible. Thus, the pretilt θ is a function of the area ratio b/a. However, for a small thickness of the mixture ($l < 10$ nm), the fourth term should be considered.

3. Experiment and Discussion

We used two polyimides, i.e., AL-00010 (JSR) for the hydrophobic medium (homeotropic PI) and SE-7492 (NISSAN) for the hydrophilic surface (planar PI) and mingled them. To improve the characteristics of the mixing, spin-coating, and alignment, three solvents (N-methylpyrrolidone, ethylene glycol butylether, and γ-butyrolactone) were added to the mixed PI. To modulate the thickness of the coated PI mixture, we adjusted the amount of solvent used. The mixture was spin-coated in two steps onto the glass substrate. The first step was performed at 1000 rpm for 10 s and the second step at 3000 rpm for 20 s. The spin-coated glass substrates were prebaked at 80 °C for 5 min, and then baked at 220 °C for 90 min on a hot plate. Here, we expect that by varying the mixing ratio of the two PIs, the surface anchoring property can be improved.

Note that, in the case of a general thickness ($l > 50$ nm) of the mixture, the surface was always almost completely hydrophobic even though the hydrophobic mixture used was of small amount.[24] This strongly indicates that the homeotropic PI is protruding out of the mixture surface and becomes dominant at the surface of the film. When an LC cell is fabricated using these film substrates, the LCs are separated completely from the hydrophilic material by the hydrophobic material. In this case, the LC pretilt changes exponentially as h varies. Most of the approaches to controlling LC pretilt angle by adjusting the mixing ratio of the mixture are considered the same as this case with a thick mixture film (about 100 nm).[14,15] This method is not suitable for a producing reproductive LC pretilt because LC pretilt angle is sensitive to mixing ratio.

To increase the processing margin for the LC pretilt, we must prevent the segregation of the two PIs in the depth direction. We propose a good idea for a pretilt generation method with high process margins. It is simply to diminish to the extreme the thickness of the mixture film. This causes the mixture to always coexist on the surface of the film, and hence the area ratio is determined only by the mixing ratio.

To examine the above concept, we prepared some LC samples fabricated on substrates and rubbed with velvet, with various mixing ratios and film thicknesses (which were controlled by adjusting the solvent concentration). The thickness of the fabricated sandwich LC cells was about 30 μm. The rubbing direction between the top and bottom substrates was antiparallel. The pretilt angle of each sample was measured by the extended crystal rotation method.[25,26] The nematic LC, i.e., ZKC-5085XX (Chisso, $\Delta n = 0.15$), was injected into each cell by capillary action. In this experiment, we set $\theta_p \approx 89°$ (AL-00010), $\theta_h \approx 5°$ (SE-7492), and $\theta_s \approx 0.5°$ (glass substrate).

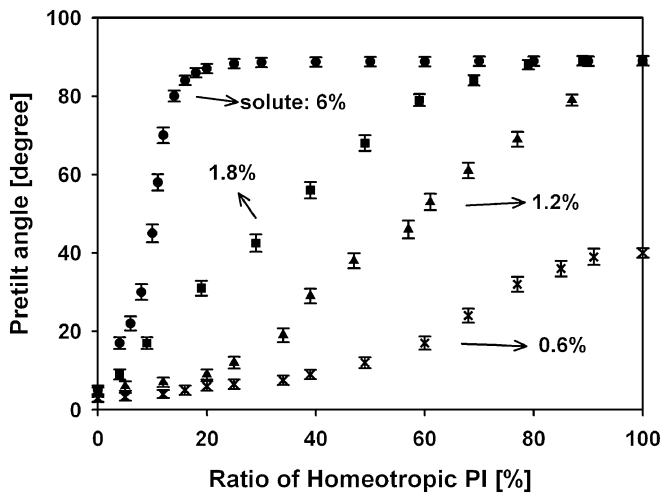Figure 2 shows the measured pretilt angle results for several mixing conditions. As expected when the mixture is

Fig. 2. Pretilt angles according to concentration ratio of homeotropic PI in various mixing condition.
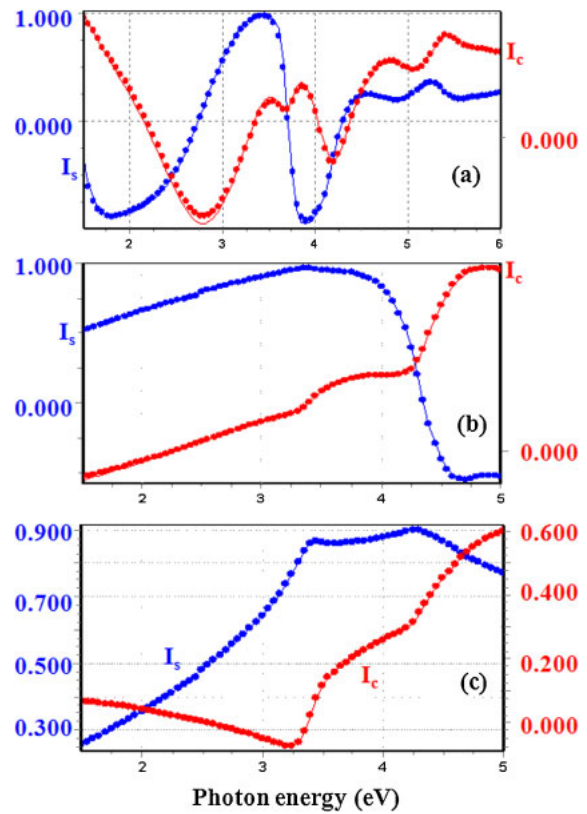

Fig. 3. (Color online) The ellipsometry results measured on the mixtures on glass substrates; (a) when the relative ratio of the homeotropic PI and homogeneous PI is 20 and 80%, respectively, and whose sum is 6% (b) when the relative ratio of the homeotropic PI and homogeneous PI is 20 and 80%, respectively, and whose sumg is 1.8% in solute (c) when the relative ratio of the homeotropic PI and homogeneous PI is 50 and 50%, respectively, and whose sum is 1.2% in solute.

thick, which we call part 1, the pretilt changes abruptly as the amount of homeotropic PI varies, as shown in Fig. 1(a). This part can be considered to be due to the phase separation region of the mixture in the depth direction (part 1). With an increase in the amount of the homeotropic PI, it becomes thick and then the interaction between the LC and the planar PI becomes rapidly weak owing to the van der Waals interactions. Therefore, when the homeotropic PIs ratio is more than 20% (thickness > 100 nm), the pretilt becomes nearly 90°. Consequently, it is not easy to produce a reliable LC pretilt in a region like part 1 owing to the thickness sensitivity of the pretilt.

When the thickness of the mixture was set to 30–60 nm, which we call part 2, the phase separation is induced partially, as shown in Fig. 1(b). Even though the two nanoscale phases coexist on the mixture surface, the process margin of the pretilt angle is insufficient since the phase separation region leading to the thickness dependence of the van der Waals interactions still exists.

When the thickness of the mixture was wet to 10–20 nm, which we call part 3, the two media mixes with almost no phase separation in the depth direction, as shown in Fig. 1(c). The pretilt will be determined only by the surface area ratio of the two media and is only slightly sensitive to the mixing ratio. We found this to be the best approach to high margin pretilt generation in a full range of angles.

When the thickness of the mixture was set below 10 nm, which we call part 4, the two media were mixed completely without any phase separation in the depth direction. This case generates a higher margin of pretilt but the pretilt range is limited owing to the very thin mixture film, which gives rise to the interaction between the LCs and the glass substrate that is generally hydrophilic.

Figure 3 shows the ellipsometry (HORIBA) results of the mixtures on glass substrates. Figure 3(a) shows the measured ellipsometry results when the relative ratios of homeotropic PI and homogeneous PI are 20 and 80%, respectively, and whose sum corresponds to solute of 6%. From the Maxwell Garnett and Bruggeman effective medium theories,[27] we concluded that the mixture is in the configuration shown in Fig. 1(a) (part 1). From this, it was found that h

and p' are 14.3 and 116 nm, respectively, and the pretilt angle of the LC cell fabricated by this sample was 87.2°. Figure 3(b) shows the measured ellipsometry results when the relative ratios of homeotropic PI and homogeneous PI are 20 and 80%, respectively, and whose sum corresponds to 1.8% of the solute. From the effective medium approximation, we can say that the mixture is in the configuration shown in Fig. 1(b) (part 2). From this we can find that h, p', and a were 8.5 nm, 27.5 nm, and 0.6, respectively. The pretilt angle was 35.3°. Figure 3(c) shows the measured ellipsometry results when the relative ratios of homeotropic PI and homogeneous PI are 50 and 50%, respectively, and whose sum is 1.2% of the solute. From the effective medium approximation, it can be concluded that that the mixture is in the configuration shown in Fig. 1(c) (part 3). From this, $h = l = p$ and a were found to be 17.5 nm and 0.63, respectively. The pretilt angle was 51°.

The solid lines shown in Fig. 4 are the results of fitting our calculations of the pretilt angle on the basis of eq. (2) to the experimental data and the results of the ellipsometry. k^{-1} and W_h/W_p can be obtained from part 1 and W_s/W_p is found from part 4. In this experiment, the fitted values of k^{-1}, W_h/W_p, and W_s/W_p are 3.2 nm, 0.33, and 3.3, respectively. The fitted values agree with the experimental values obtained using the high-voltage method,[28,29] which is very useful for measuring the polar anchoring of surface LCs.
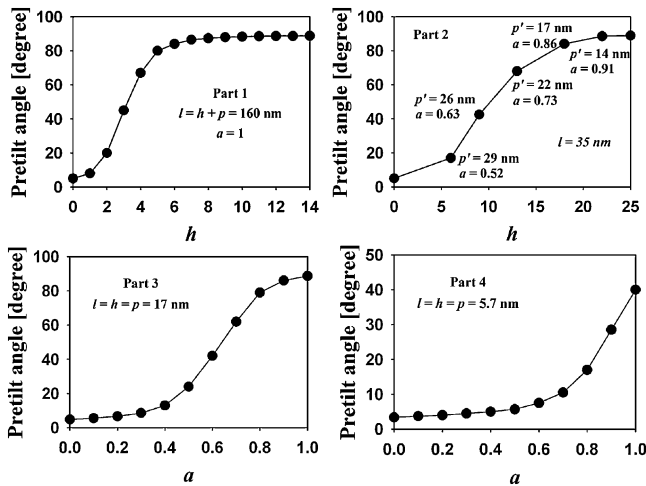
Fig. 4. The results for fitting our calculations on the experimental data of the pretilt angle based on eq. (2) and the information of the ellipsometry.

4. Conclusions

In summary, we proposed a technique for continuously controlling the pretilt angle in a wide range with a high process margin. We achieved this by tuning the thickness of a heterogeneous polyimide (PI) layer that consists of a homeotropic PI and a planar PI. The thickness of the mixture is controlled by varying the concentration of solvent. As such, the LC pretilt can be modified continuously by controlling the relative concentration ratio of the homeotropic PI and planar PI. Furthermore, we may achieve excellent reliability, uniformity, and productivity. Our simple modeling based on van der Waals interactions described the experimental results well. The fitted values of the characteristic decay length k^{-1}, W_h/W_p, and W_s/W_p were 3.2 nm, 0.33, and 3.3, respectively, when using AL-00010 as the homeotropic PI and SE7492 as the planar PI.

1) B. Jérôme and Y. R. Shen: Phys. Rev. E **48** (1993) 4556.
2) W. Chen, M. B. Feller, and Y. R. Shen: Phys. Rev. Lett. **63** (1989) 2665.
3) M. B. Ferrer, W. Chen, and Y. R. Shen: Phys. Rev. A **43** (1991) 6778.
4) B. Jérôme: Rep. Prog. Phys. **54** (1991) 391.
5) J. M. Geary, J. W. Goodby, A. R. Kmetz, and J. S. Patel: J. Appl. Phys. **62** (1987) 4100.
6) D. W. Berreman: Phys. Rev. Lett. **28** (1972) 1683.
7) J. S. Gwag, J. Fukuda, M. Yoneya, and H. Yokoyama: Appl. Phys. Lett. **91** (2007) 073504.
8) J. S. Gwag, M. Yoneya, H. Yokoyama, and J.-H. Kim: Appl. Phys. Lett. **92** (2008) 153110.
9) J. S. Gwag, J. H. Kwon, M. Oh-e, J.-I. Niitsuma, M. Yoneya, and H. Yokoyama: Appl. Phys. Lett. **95** (2009) 103101.
10) S. Faetti, M. Gatti, V. Palleschi, and T. J. Sluckin: Phys. Rev. Lett. **55** (1985) 1681.
11) P. Chaudhari and L. James: Nature (London) **411** (2001) 56.
12) J. S. Gwag, C. G. Jhun, J. C. Kim, T.-H. Yoon, G.-D. Lee, and S. J. Cho: J. Appl. Phys. **96** (2004) 257.
13) M. Schadt, H. Seiberle, and A. Schuster: Nature (London) **381** (1996) 212.
14) F. S. Yeung, J. Y. Ho, Y. W. Li, F. C. Xie, O. K. Tsui, P. Sheng, and H. S. Kwok: Appl. Phys. Lett. **88** (2006) 051910.
15) J. Y. Ho, V. G. Chigrinov, and H. S. Kwok: Appl. Phys. Lett. **90** (2007) 243506.
16) B. Zhang, F. K. Lee, O. K. Tsui, and P. Sheng: Phys. Rev. Lett. **91** (2003) 215501.
17) J. B. Kim, K. C. Kim, H. J. Ahn, B. H. Hwang, D. C. Hyun, and H. K. Baik: Appl. Phys. Lett. **90** (2007) 043515.
18) J. B. Kim, K. C. Kim, H. J. Ahn, B. H. Hwang, J. T. Kim, S. J. Jo, C. S. Kim, H. K. Baik, C. J. Choi, M. K. Jo, Y. S. Kim, J. S. Park, and D. Kang: Appl. Phys. Lett. **91** (2007) 023507.
19) J. L. Janning: Appl. Phys. Lett. **21** (1972) 173.
20) M. Nakamura and M. Ura: J. Appl. Phys. **52** (1972) 210.
21) J. N. Israelachvili: *Intermolecular and Surface Force* (Academic Press, London, 1991) Chap. 11, p. 199.
22) K. H. Yang and C. Rosenblatt: Appl. Phys. Lett. **43** (1983) 62.
23) H. Yokoyama and H. A. van Sprang: J. Appl. Phys. **56** (1984) 2645.
24) J. S. Gwag, M. Oh-e, M. Yoneya, H. Yokoyama, H. Satou, and S. Itami: J. Appl. Phys. **102** (2007) 063501.
25) J. S. Gwag, S. H. Lee, K.-H. Park, W. S. Park, K.-Y. Han, C. G. Jhun, T.-H. Yoon, J. C. Kim, D.-M. Song, and D.-M. Shin: J. Appl. Phys. **93** (2003) 4936.
26) S. B. Kwon, K. Y. Han, and T. Uchida: J. Inst. Image Inf. Telev. Eng. **18** (1994) 13.
27) G. A. Niklasson, C. G. Granqvist, and O. Hunderi: Appl. Opt. **20** (1981) 26.
28) H. Yokoyama and H. A. van Sprang: J. Appl. Phys. **57** (1985) 4520.
29) A. Sugimura, T. Miyamoto, M. Tsuji, and M. Kuze: Appl. Phys. Lett. **72** (1998) 329.