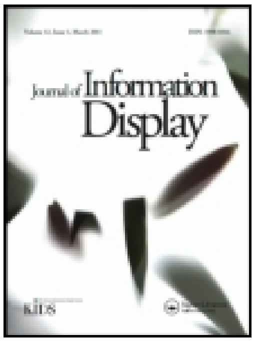

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Vertical Alignment of Liquid Crystals by Ordering Effect of Self-assembled Monolayers on the Ion-beam-irradiated Anisotropic Surface

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Abstract

In this paper, vertically aligned (VA) liquid crystal (LC) modes were investigated using the alkyl chain ordering effect of self-assembled monolayers (SAMs) prepared on the anisotropic inorganic surface. On the anisotropic surface prepared through oblique ion beam irradiations, the SAM molecules are adsorbed, producing macroscopic alkyl chain ordering, which can determine the pretilt direction of the vertically aligned LC molecules through the intermolecular interactions on the surface.

Keywords: self-assembled monolayer, dodecyltrichlorosilane, liquid crystal, vertical alignment, ion beam

1. Introduction

With the development of the liquid crystal display (LCD) technology, several studies are being conducted to solve the conventional problems of LCDs, such as their limited viewing angle and slow response time. The limited-viewing-angle problem is very critical in the vertically aligned (VA) LC mode because the uniform-field-induced reorientations of the LC molecules induce severe birefringence variation depending on the incident angle of the beams. Therefore, VA modes employ multidomain LC geometries for wide-viewing-angle properties, which include a patterned VA (PVA) mode [1, 2] using patterned electric fields from patterned electrodes, and a multidomain VA (MVA) mode [3] using a patterned surface pretilt from the patterned protrusions. These methods, however, produce patterned LC orientations from the patterned subpixel boundaries and not from the surface over the whole pixel area; thus, the improvement of the response time property is highly limited due to the complex LC dynamics induced from the reverse-tilting domains before stabilization. Recently, to obtain fast-switching LC dynamics, alternative multidomain VA methods were proposed, which include a mixed patterned surface using a combination of patterned planar LC alignment and VA surfaces [4-6] or optically/electrically patterned LC alignments using a mixture of LCs and photocurable liquid crystalline monomers [7]. These multidomain methods have problems, however, such as LC alignment instability and a complex fabrication process. Therefore, a new LC alignment method is required to overcome these demerits.

In this paper, an alkylsiloxane self-assembled-monolayer (SAM) [8] ordering effect produced by the anisotropy of the underlying SiO_2 surface [9] was proposed to obtain a multidomain VA LC geometry, where the LC molecules were directly aligned by the ordered SAM layer. Here, patterned oblique ion beam irradiations were used to transform the SiO_2 surface into an anisotropic interface. Through SAM treatment, the planar LC anchoring surface of the ion-beam-irradiated SiO_2 surface could be easily changed into a homeotropic LC anchoring surface. In addition, the patterned pretilts for the multidomain VA LC geometry were spontaneously obtained depending on the SiO_2 surface conditions. The thermal stabilities of the SAM layer were analyzed to investigate the dominant factors affecting the LC alignments on the SAM surface.

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2. Experiment

SAM is an organic monolayer formed through the adsorption of an active surfactant on a solid surface. It consists of a head group, a flexible chain, and an end group. Head groups selectively combine with the substrate, flexible chains form an ordered molecular layer due to the steric effects of molecular interactions at a high SAM packing density, and end groups determine the functions of the layer surface. Depending on the functionality of the end group, SAMs have been widely used in several fields, such as MEMS, molecular/organic electronics, biochips, and the soft-lithographic patterning process [10-18]. When the end group is composed of CH3, the SAM surface aligns the LC molecules homeotropically due to the hydrophobic-surface effects [19-21]. It was reported that the SAM layer could determine the pretilt direction of LC anchoring due to the intermolecular interaction between the ordered flexible alkyl chains and the LC molecules when the SAM layer was ordered by direct rubbing [22] or plasma beam irradiation [23] on the SAM surface. These methods, however, can produce SAM defects via desorption during treatments. In addition, the rubbing method is not suitable for the multi-domain LC modes. Here, the macroscopically ordered SAM surface, prepared by modifying the underlying surface anisotropically, was first demonstrated. A DDTS (dodecyltrichlorosilane) alkyl-siloxane SAM was used for the SAM molecule, and a transparent SiO_2 for the SAM binding surface.

For the fabrication of LC cells, indium tin oxide (ITO) glasses were cleaned with acetone, isopropyl alcohol, and deionized water. For chemical bonding with the substrate and the head molecules of the alkylsiloxane SAMs, 500-nm-thick SiO_2 was deposited on the prepared ITO glasses via PECVD, at 300°C (726 Å/min), except for the electrode parts. Before the SAM treatment, SiO_2 substrates with a different anisotropy were prepared by varying the oblique ion beam irradiation conditions. For the alkylsiloxane SAM treatment of the modified SiO_2 surface, DDTS SAM solution (1 wt%) was used with anhydrous toluene on the 50°C hot plate, for 4 h. All the SAM treatments were processed in a glove box filled with nitrogen gas. The SAM-treated substrates were cleaned in toluene for 3 min and were then baked on a 90°C hot plate for 20 min. Initially, the SiO_2 surface showed a hydrophilic-surface property, but the surface was transformed into a hydrophobic surface after DDTS SAM treatment, as shown in the contact angle results in Fig. 1. The surface energy change from the hydrophilic to the hydrophobic state was due to the hydrophobic end group of the SAM molecules (-CH_3). The amount of the contact angle after the SAM treatment shows the coverage density of SAM, which is comparable with the results obtained in previous researches [10-15], and shows that the SAM layer herein has an almost-full-coverage density.

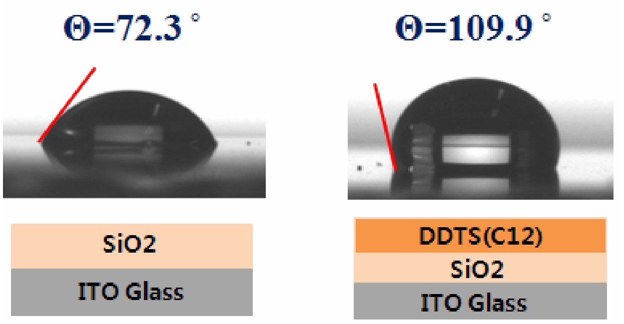


Fig. 1. The contact angle results before and after DDTS SAM treatment on the SiO_2 surface.

Two types of SAM-treated substrates were prepared: (sample 1) the DDTS-SAM surface on the non-rubbed, isotropic SiO_2 substrate, and (sample 2) the DDTS-SAM surface on the ion-beam-irradiated anisotropic SiO_2 substrate. For sample 2, the ion beam irradiation condition was set to a planar LC alignment condition because such condition has better thermal stability, and because the ion beam irradiation condition is also easily chosen therein, with a large process margin, compared with the homeotropic LC alignment condition from ion beam irradiation. Samples 1 and 2 were fabricated by assembling the SAM-treated substrates using a 6-µm spacer. The LC anchoring properties were checked with the LC textures through a polarizing optical microscope, depending on the applied voltages. The dielectric anisotropy of the LC was $\Delta\varepsilon = -3.8$ in all the cases.

In addition, a polarizing microscope was used to see the LC textures after annealing, and the thermal stability of the SAM layer was analyzed to determine the dominant factors affecting the LC alignment on the SAM surface. In this case, the annealing temperature increased by 10°C step by step, starting from 100°C, until the pretilt of the LC anchoring disappeared. The LC textures were observed at room temperature after cooling down the sample. The annealing time was 1 h at each temperature condition.

3. Experiment Results

Fig. 2 shows the LC textures by VA effects of the SAM prepared on the isotropic SiO_2 surface. In the field-off states, the LC textures showed completely dark states regardless of the sample rotations, which means that the LC molecules are vertically aligned on the SAM surface due to the hydrophobic effects of the SAM end group. In the field-on state, however, the LC reorientations perpendicular to the electric field were shown to be random planar, which is called “Schlieren texture”. Fig. 2 shows that there is no preferential pretilt direction in LC anchoring in the case of normal SAM treatment. In other words, SAM ordering, produced only by the intermolecular interaction between the SAM molecules, is polydomain ordering and not macroscopic SAM ordering, which cannot provide the preferential easy axis in LC anchoring.

Fig. 3(b) shows the LC textures by the VA effects of the SAM prepared on an ion-beam-irradiated anisotropic SiO2 surface. Fig. 3(a) shows that before the SAM treatment, the LCs were aligned on the SiO_2 surface with homogeneous planar anchoring due to the anisotropy of the SiO_2 surface induced by the ion-beam irradiation. After the SAM treatment, the LC texture showed a completely dark image in the field-off state due to the hydrophobic effect of the SAM surface, as in sample 1. In addition, this texture showed that an atomic defect, which can be produced during ion-beam irradiation, is negligible in SAM binding with an ion-beam-treated SiO_2 surface. In the field-on state, however, the LC texture showed a uniform bright state. This means that the preferential easy axis as well as the pretilt is produced on the SAM surface by the irradiation of the ion beam on the underlying SiO_2 surface. The pretilt direction is parallel to the ion beam irradiation direction. It can be seen in Fig. 3 that a macroscopically well-ordered SAM surface can be produced by modifying the underlying SAM-binding surface into an anisotropic surface, and that the bottom-up ordered SAM surface can determine the pretilt direction in LC anchoring.

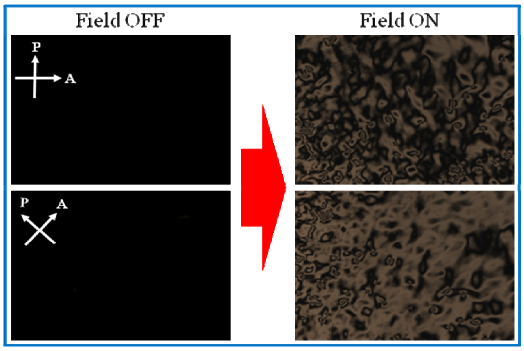
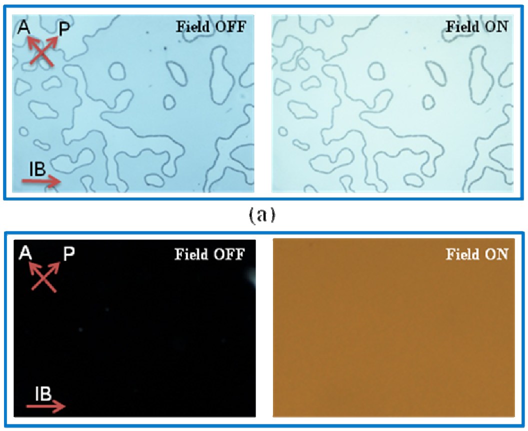


Fig. 2. The polarizing microscopic LC textures of sample 1 (LC aligned on the SAM surface promoted on isotropic SiO_2).



(a)

(b)

Fig. 3. The polarizing microscopic LC textures: (a) the LC textures on the ion-beam-irradiated SiO_2 before SAM treatment; and (b) the LC textures after DDTS-SAM treatment on the ion-beam-irradiated SiO_2 surface.

As for the reason for the pretilt inducement on the SAM surface prepared on the anisotropic SiO_2 surface (sample 2), three mechanisms can be proposed. The first is that LC is oriented by the molecular interaction between the alkyl chains of the ordered SAM molecules and the LC molecules. The ordering state of the SAM directly affects the LC alignment. The SAM is formed with a tilting angle due to the underlying surface morphology, and then the LCs on the SAM are affected by the tilted SAM. The second is that the LC is aligned by the competition effects between the planar anchoring from the ion-beam-irradiated underlying SiO_2 surface and the homeotropic anchoring from the partially covered hydrophobic SAM surface. Here, the pretilt is determined by the relative coverage effects. The third and final mechanism concerns the partial screening effects of the thin SAM layer from the dipole moments existing in the ion-beam-irradiated SiO_2 surface. The high energy of the ion beam can break the atomic structure, which will produce dipoles on the SiO_2 surface. Actually, the aforementioned three mechanisms would co-exist in the SAM surface herein for LC anchoring.

To determine which mechanism is dominant for the LC alignment effects on the SAM surface, the LC textures after thermal annealing using sample 2 were observed. Fig.

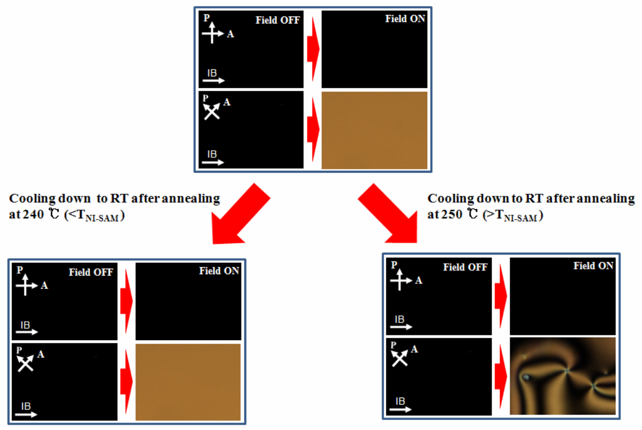


Fig. 4. The polarizing microscopic LC textures obtained after thermal treatments.

4 shows the LC textures at room temperature after fast cooling followed by the annealing process. In both cases, which had different annealing temperature conditions, the LC textures showed completely dark images in the field-off state, which means that the desorption effects of the SAM are negligible within the annealing temperature conditions herein. In the field-on states, however, the LC textures differ according to the annealing temperature conditions. When the annealing temperature was 240°C for 1 h, the LC texture did not change, but when the annealing temperature was increased to 250°C, the LC texture was shown to be a Schlieren texture, which means that the SAM layer was disordered by the thermal treatment. Here, the annealing time was the same. These results show that the ordering transition temperature of the SAM layer ($T_{NI\text{-}SAM}$) exists between the two annealing temperatures. Under the cell condition, the nematic-to-isotropic-phase transition temperature of the LCs ($T_{NI\text{-}LC}$ ~ 70°C) is much lower than $T_{NI\text{-}SAM}$. When the annealing temperature is lower than $T_{NI\text{-}SAM}$, the pretilt effect still exists in the SAM surface after cooling down to room temperature while the annealing temperature increases, exceeding $T_{NI\text{-}SAM}$, which signifies that the SAM ordering has been interrupted. These results mean that the direct molecular interaction between the LC molecules and the ordered SAM alkyl chain is dominant in the LC pretilt formation.

Fig. 5 shows the structure of the SAM ordering and the schematic diagram of the LC alignments according to the SAM condition. When SAM is formed on the isotropic surface, SAM ordering exists just within the microdomains. Thus, the LC textures are shown to be Schlieren textures, as shown in Fig. 2, and the sample is over $T_{NI\text{-}SAM}$ in Fig. 4, as shown in Fig. 5(a). The results shown in Fig. 3 were obtained through the bottom-up promotion of the macroscopic SAM ordering, as shown in Fig. 5(b).

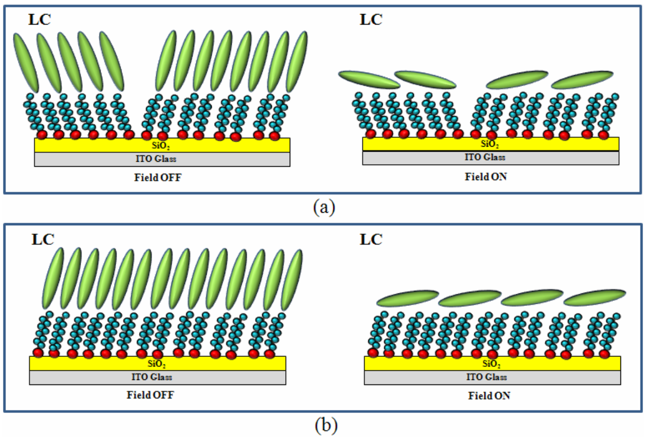


Fig. 5. Structure of a SAM, and schematic diagram of the LC alignment on the SAMs: (a) LC alignment on the SAM with polydomain ordering prepared on an isotropic SiO_2 surface; and (b) LC alignment on the SAM with macroscopic monodomain ordering prepared on an anisotropic SiO_2 surface.

4. Conclusion

It was shown that the VA effects of SAM depend on the anisotropy of the underlying inorganic SiO2 surface. The hydrophobic SAM surface aligns the LC vertically in the field-off state, irrespective of the anisotropy of the underlying surface. When the underlying surface is anisotropic, the LC anchoring on the SAM surface produces the pretilt property due to the macroscopic SAM ordering effects. The thermal-treatment experiments showed that the LC pretilt formation on the SAM surface is produced predominantly by the molecular interaction between the LC molecules and the ordered SAM alkyl chains. The obtained results show that the patterned VA mode can be simply prepared via SAM treatment on the patterned anisotropic surface only if the underlying surface is chemically available for SAM binding.

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