Soft-lithography for preparing patterned liquid crystal orientations

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Abstract

We demonstrate novel soft-lithographic techniques for preparing patterned liquid crystal (LC) orientations at an alignment layer. By controlling patterning conditions such as wetting property and operating temperature depending on polymeric materials, multi-directional or modified LC alignment conditions can be simply achieved.

1. Introduction

Recently, several types of multi-domain liquid crystal (LC) structures have been proposed to enhance or modify electro-optic (EO) properties of LC-based devices. In LC displays (LCDs), conventional viewing angle problems can be solved by azimuthally distributed LC orientations [1,2]. In transflective LCDs, the amount of retardation in transmissive and reflective parts can be tuned by controlling surface pretilt of LCs differently in each part [3]. Electrically controllable, diffractive LC devices are achieved by periodically modified LC orientations [4].

Since LC structure in bulk is determined by surface alignment condition, patterned LC alignment layer is essentially required in obtaining multi-domain LC structures. As patterning methods to modify LC anchoring spatially, mechanical scribing methods with atomic force microscope tip [5] or metallic ball sphere [6,7] and optical alignment methods with photosensitive materials [8,9] have been proposed. However, such conventional approaches are not attractive for real applications due to their complex procedures requiring long processing time or their low stability in LC anchoring.

In this paper, we demonstrated novel soft-lithographic techniques for preparing patterned LC orientations at an LC alignment layer. First, we proposed a micro-contact printing method with conventional polyimide (PI) materials by facilitating surface wetting properties of the patterning PIs between the mold surface and the base surface to be patterned. With the micro-contact printing method, PI layers can be easily stamped on an ITO substrate or a different PI surface. Secondly, we proposed a pressure-assisted capillary force lithography (PA-CFL) method by patterning thermoplastic polystyrene (PS) layers on a thermally

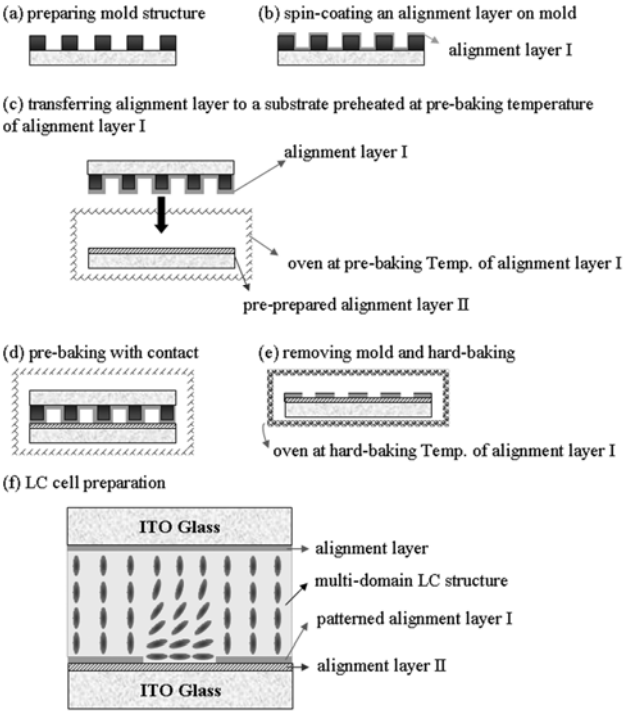

Figure 1. The schematic illustrations of LC alignment layer patterning procedures with micro-contact printing method.

stable PI layer. On the patterned PS/PI surface, the LCs are aligned orthogonally with producing multi-domain LC structures due to different easy axis generation after unidirectional rubbing process.

2. μ-Contact printing method

Figure 1 shows the proposed alignment layer patterning procedures with micro-contact printing method. First, a patterning material (PI I) was spin-coated on a patterned mold structure. As a base substrate to be patterned, a bare ITO substrate or other PI-coated susbtrate was prepared. The base substrate was pre-heated to a pre-baking temperature of the patterning material (PI I). Then, the PI-coated mold substrate was placed on the heated base substrate. If the wettability of the patterning material on the base substrate is higher than that on the mold surface, the PI I on the mold surface is transferred to the base substrate with the patterns of the mold structure during this first baking process. The imidization of the PI was executed after removing the mold structure from the base substrate. Finally, the patterning of alignment layers was completed. When the second baking process for PI imidization was executed with preserving the contact, we could not obtain uniform pattern transfer of PIs from the mold surface to the base film surface due to increased adhesion of imidized PI on the mold surface. Therefore, the pattern transfer should be executed in solvented state of PIs as shown in Fig. 1.

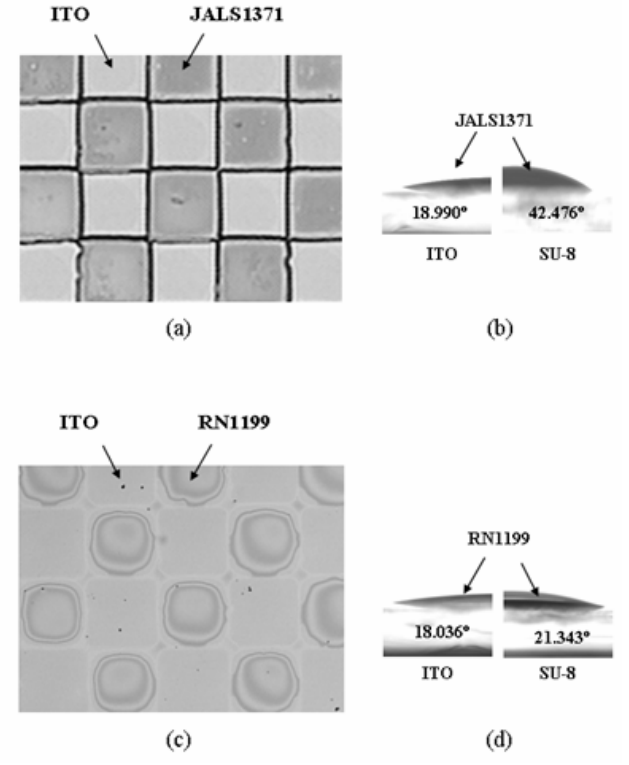

Figure 2. Micro-contact printed planar LC alignment PI layer on ITO surface. (a) and (c) are the microscopic images of JALS1371 and RN1199 patterns, respectively, on an ITO surface. (b) and (d) are the contact angles of JALS1371 and RN1199 in solvented states, respectively, on the ITO base surface and the SU-8 mold surface.

A patterned mold substrate was fabricated by a photo-lithographic method using negative photoresist of SU-8 (MicroChem). As patterning materials, commercially available PIs, AL1H659 (JSR Co.), RN1199 (Nissan Chemical Ind.), and JALS1371 (JSR Co.) were tested, where AL1H659 was a homeotropic LC alignment PI and both RN1199 and JALS1371 were planar LC alignment PIs. The PIs were patterned on a bare ITO surface or other PI surfaces.

The patterned planar LC alignment PI (JALS1371 and RN1199) layers on an ITO surface were presented in Fig. 2. The patterned substrates were prepared by micro-contact printing with identical SU-8 mold substrate in 100 μm period of check patterns. Figures 2 (a) and (c) shows that JALS1371 pattern on the ITO surface was obtained with good uniformity, whereas the RN1199 pattern on the ITO surface was highly irregular one. When we used RN1199 as a patterning

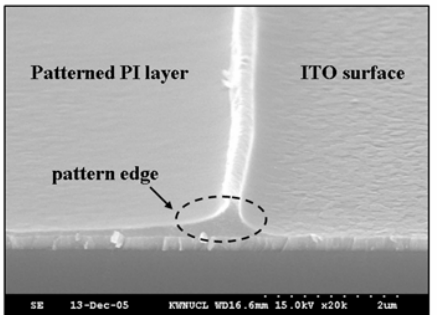

Figure 3. The cross-sectional SEM image of the patterned PI (JALS1371) layer on the ITO surface.

PI material, it was observed that much of RN1199 were still remained on the mold surface. Above results can be explained by the relative wettability of patterning materials between on the mold surface and the base surface as shown in Figs. 2 (b) and (d). The contact angles of RN1199 showed similar values, whereas the contact angle of JALS1371 on the SU-8 was more than two times of that on the ITO surface. This relative surface wettability of the patterning PIs resulted in the different pattern uniformity between JALS1371 and RN1199 in our experiment.

Figure 3 shows the cross-sectional SEM image of the patterned PI (JALS1371) layer on the ITO surface, where we could observe the selectively patterned PI layer only in the micro-contact printed area by the mold structure. The boundaries of the PI patterns were relatively thicker than the inner areas of the pattern since some of patterning PIs were squeezed out from the patterning area during the micro-contact procedures. Such phenomena are expected to be reduced by optimizing our micro-contact printing procedure but they could not be completely solved. Therefore, micro-contact printing method would be limited in pattern resolution about hundreds of micrometer scale.

With the micro-contact printing method, we fabricated patterned a homeotropic/planar LC alignment layer with AL1H659 and RN1199. When we used RN1199 as a patterning PI and AL1H659 as a base PI layer, patterning material was more wettable on the mold surface than on the base surface, as shown in Fig. 4. Therefore, the RN1199 on the SU-8 mold surface was partially transferred to the AL1H659 surface. However, in reverse case, AL1H659 on the mold surface could be easily

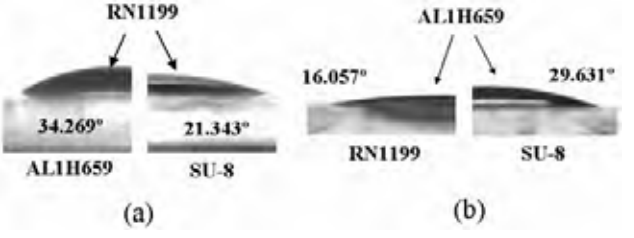

Figure 4. The contact angles of (a) RN1199 on AL1H659 and SU-8 surfaces and (b) AL1H659 on RN1199 and SU-8 surfaces.

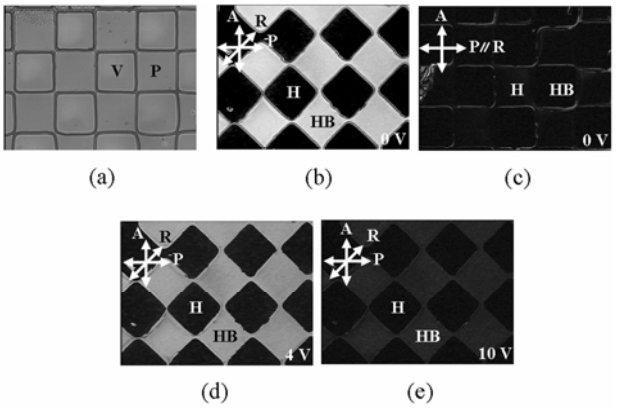

Figure 5. (a) The microscopic image of the patterned homeotropic LC alignment PI (AL1H659) layer on the planar LC alignment PI (RN1199) layer. (b), (c), (d), and (e) are the polarizing microscopic images of the LC ($\Delta\varepsilon>0$) cell with two domains of the homeotropic (H) and the hybrid (HB) geometries, which is produced by assembling the patterned substrate of (a) with the other substrate uniformly coated by the homeotropic LC alignment layer. (b) and (c) are obtained in the absence of an applied voltage. (d) and (e) are obtained in the presence of applied voltages of 4 V and 10 V, respectively.

transferred to the RN1199 base surface and we could obtain uniform pattern transfer.

With the patterned LC alignment substrate and an unpatterned planar LC alignment substrate, we made a LC cell by anti-parallel rubbing on both surface and filling LC with a positive dielectric anisotropy. In this cell structure, the different LC anchoring effect in pretilt angle at two domains could be obviously observed in the presence of applied voltages. The polarizing microscopic images of Fig. 5 (b) and (c) obtained in the absence of an applied voltage showed that our cell had two LC domains with homeotropic and hybrid configurations. In the field-on state, the transmittance of the only hybrid region on the RN1199 was decreased with increasing applied voltages and the textures were uniformly changed. The homeotropically aligned LCs on the patterned AL1H659 surface showed no light leakage irrespective of applied voltages. The above results showed that the patterning material AL1H659 was transferred precisely on the base substrate of RN1199

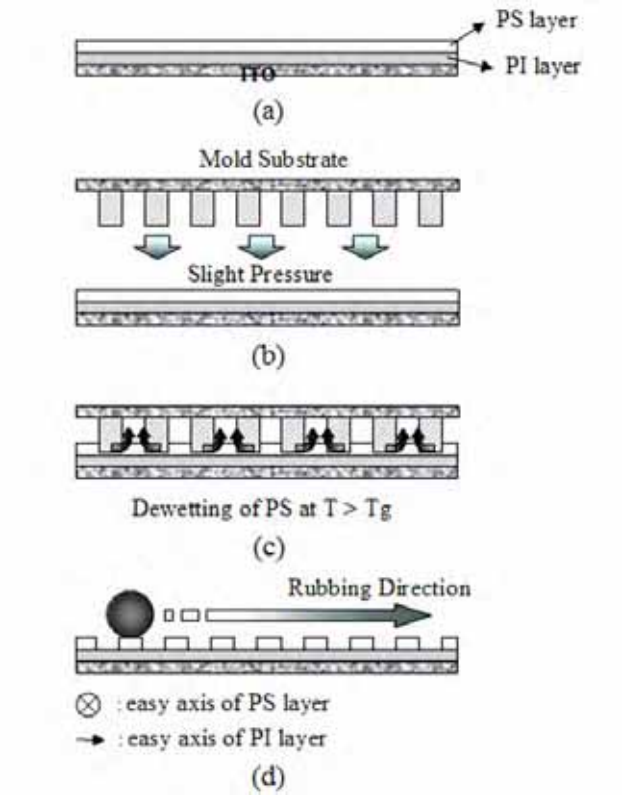

Figure 6. The schematic illustrations of pressure-assisted capillary force lithographic procedures for patterning LC alignment layers.

with producing patterned surface anchoring conditions in LC tilt.

3. Pressure-Assisted capillary force lithography method

Figure 6 shows the pressure-assisted capillary force lithographic patterning of LC alignment layers for producing multi-directional easy axis distribution. In this patterning, we used different thermal stability and different rubbing-induced easy axis generation between PI and PS. First, a PI layer and a PS layer were sequentially spin-coated as shown in Fig. 6 (a). A homogeneous LC alignment PI, RN1199 was used for the thermally stable base polymer film. As a patterning material, a thermoplastic isotatic PS (i-PS, Scientific Polymer) diluted in toluene was spin-coated on the PI film. Then, a photo-lithographically fabricated, patterned mold structure was contacted on the prepared bilayer polymer films. Then, the combined substrates were heated above the glass

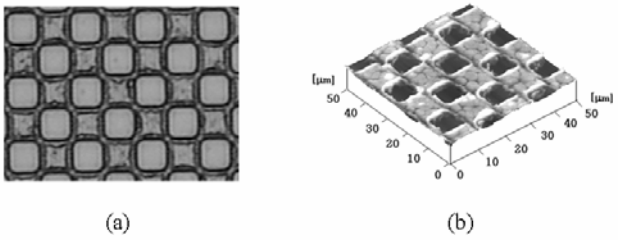

Figure 7. (a) Microscopic image of PS patterns on the PI layer and (b) 3-dimensional AFM image.

transition temperature ($T_g \cong 100^{o}$C) of the i-PS and the mold substrate was slightly pressed down to achieve conformal contact as shown in Fig. 6 (b). During this procedure, the PS film became melted state and the mold structure sank down to the PI layer. The i-PS in the areas where the mold structure was closest to the base substrate was dewetted from the PI layer and was filled into the mold spacing areas by pressure-assisted capillary filling. After the dewetting process was fully completed, the substrates were cooled down to room temperature and then the mold was removed carefully. Finally, PS patterns on the PI layer were obtained in reverse structure of the mold pattern.

Figure 7 shows the patterned PS layer on the PI layer. In our thermal treatment, only PS was melted and patterned by the mold structure. The PS patterns were obtained with SU-8 mold structure with 10 μm square patterns. Comparing with the micro-contact printing method, the PA-CFL method had an advantage that higher resolution patterns could be obtained and the soft-lithographic procedures were not affected by the solvent types of the used patterning materials. The thickness of the patterned PS layer was about 200 nm.

When the patterned substrate was unidirectionally rubbed, the LCs on the PI layers were aligned along the rubbing direction, whereas the LCs on the PS layers were perpendicular direction to the rubbing direction. This originated in the different reorientation of the side chains, where the side chains of PIs and i-PSs were realigned parallel and perpendicular to the rubbing direction, respectively.

We produced 10 μm PS line patterns on the PI layer with the PA-CFL method. The patterned substrate was assembled with unpatterned PI layer. Two substrates were rubbed orthogonally each other as shown in Fig. 8 (a). Into the cavity, a nematic LC

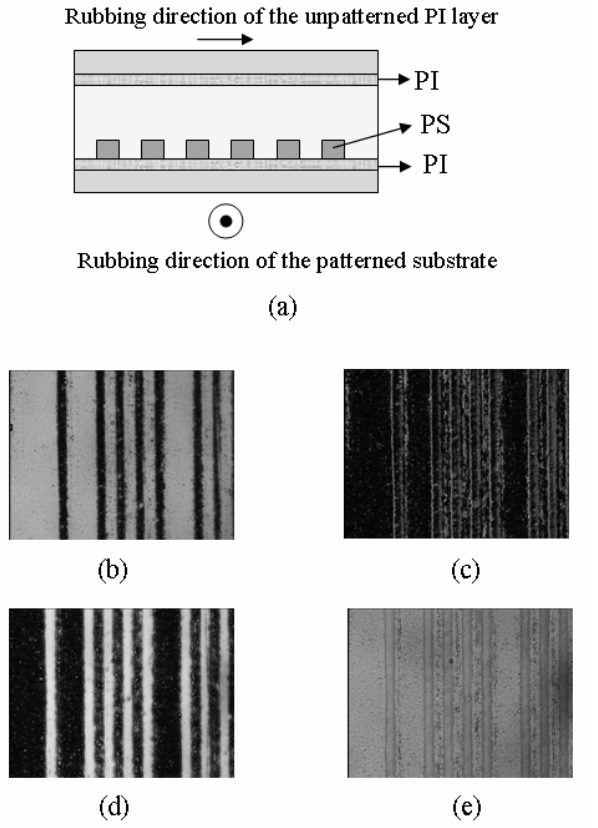

Figure 8. (a) Multi-domain LC cell structure by patterned PS/PI layer and the unpatterned PI layer. (b) and (c) are the polarizing microscopic images of the LC cell obtained under the crossed polarizers at applied voltages of 0 V and 10 V, respectively. (d) and (e) are the polarizing microscopic images obtained under the parallel polarizers at applied voltages of 0 V and 10 V, respectively.

(NLC) with positive dielectric anisotropy was filled in an isotropic temperature of LC. In our experiment, T_{NI} of the NLC was lower than T_g of the i-PS, thus the patterned PS did not be affected by the thermal treatment during the LC filing. Figure 8 (b) and (c) shows the polarizing microscopic textures under the crossed polarizers at an applied voltage of 0 V and 10 V, respectively. On the patterned PS layers, the LCs had a homogeneously planar structure, where dark state was obtained. On the patterned PI layer, the LCs had a twisted nematic structure, where bright state was obtained. When we increased the applied voltage, the LC textures on the patterned PI layer became dark state, whereas the LC texture on the patterned PS layer did not show any change. When we changed polarizer conditions from the crossed polarizers to parallel polarizers, the dark and the bright state were changed in each region. When we increased the applied voltage, all the regions were changed to bright state. The above results meant than the LCs on the patterned PS regions were aligned perpendicular to the rubbing direction and those on the patterned PI regions were aligned parallel to the rubbing direction. In addition, 10 μm PS line patterns on the PI layer were successfully obtained in our experiment.

4. Conclusion

We proposed a patterning method of LC alignment layers for generating multi-domain LC structure. By micro-contact printing conventional PI layers or patterning PS on a PI layer by PA-CFL method, LC alignment layers were patterned with spatially varying pretilt or azimuthal easy axis of LC anchoring. Such patterning was achieved by applying proper patterning methods depending on the patterning conditions and patterning materials. Our methods are expected to be very useful tools in enhancing or designing EO properties of LC-based devices requiring multi-domain LC structures.

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