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PAPER

Homeotropic alignment of liquid crystals on a nano-patterned polyimide surface using nanoimprint lithography

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In this paper, nanoimprint lithography was utilized to transfer a nano-pattern (NP) onto a homeotropic polyimide (PI) surface for use in liquid crystal displays (LCDs). The nano-patterned silicon mold was fabricated by laser interference lithography. A NP PI layer acted as the homeotropic alignment layer to easily and uniformly align the liquid crystal (LC) molecules. A NP LC cell with a NP PI layer was successfully operated as a vertical aligned LCD, and its performance was evaluated. The threshold voltage and response time of the NP LC cell were 2.472 V and 22.7 ms, respectively. In addition, the NP LC cell was characterized by a high thermal budget. Therefore, the competitive performance of the NP LC cell could allow new approaches to replace the conventional rubbing process in display technology.

1. Introduction

Aligning liquid crystal (LC) molecules on stable and uniform layers is essential for the fabrication of high-quality liquid crystal displays (LCDs). To align LC molecules, the alignment surface of the substrate is reformed to provide anchors for the LC molecules. Many techniques for anchoring LC molecules on the surface of alignment layers have been reported.^{1–9} Generally, polyimide (PI) is used in LC cells as an alignment layer by a mechanical rubbing process, which generates micron sized parallel grooves using a rubbing roller.² Recently, a number of alignment methods have been proposed as potential replacements for the rubbing process, such as the oblique evaporation method,⁵ photo-alignment method,^{6,7} and ion beam alignment methods.^{8–11} However, these methods are rarely cost effective due to complexity. As an alternative, LC molecules can also be aligned by employing specific surface topographies, which can be created by various methods.^{12–16} The alignment of LC molecules by microscale or nanoscale patterns allows more freedom in the control of alignment properties (*i.e.*, pretilt angle, anchoring energy, and multistability) than conventional methods.

Among the various techniques to fabricate nanoscale patterns, laser interference lithography (LIL) allows the production of periodic nano-size structures, quickly, uniformly, and in large areas. The advantage of LIL technique is that it is a relatively simple and fast process, and the exposure and development steps

can be completed in a few minutes making it well-suited for high throughput production. It can fabricate well ordered nano-patterns on a flat surface and easily control the pitch length and height of features.

In addition, nanoimprint lithography is a simple, low cost process with high throughput and high resolution for the fabrication of topographic patterns. These advantages make it a more attractive option than e-beam lithography and atomic force microscopy (AFM) scratching. Nanoimprint lithography can also produce substantially smaller length scales and deep patterns. Nanoimprint lithography is the most promising candidate for large scale patterning of micro-/nanostuctures on surfaces, and its attractiveness is further enhanced by its simplicity.

Previously, J. S. Gwag *et al.* created nanoscale two-dimensional surface grooves on substrates by nanoimprint lithography using e-beam lithographic mold for functional LC alignment.^{17–19} H. Takahashi *et al.* also investigated the alignment of LC molecules using ultrafine nanogrooves fabricated by e-beam and nanoimprint lithography.²⁰ H. J. Kim *et al.* fabricated nanoscale grating patterns with indium-tin-oxide (ITO) and indium-zinc-oxide (IZO) by ultraviolet nanoimprint technique and sputter deposition process as conducting electrodes for LC devices.^{21,22} On the other hand, Shishido *et al.* reported the behavior of LC molecules in a two dimensional periodic structure constructed by LIL.²³ However, there has been no study on LCD applications using nanoimprint lithography with laser lithographic nano-patterned mold for simple and fast processes.

In this study, we used nanoimprint lithography to form a grating nanopattern (NP) with dimensions of about 350 nm, and then employed these structures as LC alignment layers for LCDs. To generate a silicon mold for nanoimprint lithography, an NP was etched by using LIL, a maskless, quick process

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covering a large area using a simple apparatus.²⁴ We demonstrated that LC molecules can be aligned using this topographic pattern, which is confirmed by measurements of the electro-optical behavior of the LC molecules. This technique is expected to be very useful for achieving convenient and uniform alignment of LC molecules.

2. Experimental

Fig. 1 illustrates the procedures for nanoimprint lithography using a silicon mold fabricated by the LIL process and the fabrication of LC cells with NP alignment layers. To generate a complete grating nanostructure for the silicon mold, we used deep-ultraviolet LIL.²⁴ A single beam Lloyd's mirror interferometer was used in conjunction with an Ar-ion ($\lambda = 257$ nm) laser light source. By applying a 257 nm wavelength laser, higher resolution can be achieved and faster exposure becomes possible, with the availability of higher power. The laser with 515 nm wavelength was frequency doubled by beta-barium borate crystal. The laser beam goes through the spatial filter which was then expanded 27 times. A pinhole was applied for noise reduction and an iris for the exposure beam area selection. The applied exposure intensity varied between 15 mJ cm^{-2} , controlled by the optical power/energy meter (Newport, 1936-C) at 110 s. Using LIL, a NP structure with a 380 nm period was fabricated onto the silicon substrate ($1.5 \times 1.5 \text{ cm}^2$). The silicon mold can be used directly as a template for generating a grating nanopattern. To prepare a polymer replica of the mold, ITO coated glass substrates were cleaned supersonically in a trichloroethylene–acetone–methanol–deionized water solution for 10 min and were

then dried with N_2 gas. Homeotropic PI was chosen as a patterned polymer material for LC alignment. Homeotropic PI (JALS-696-R2, JSR Co. Ltd) was uniformly spin-coated on ITO-coated glass, then imprinted with the silicon mold, and was then imidized at 220°C for 1 h. The NP alignment substrates were fabricated in an antiparallel configuration with a cell gap of $60 \mu\text{m}$ and $5 \mu\text{m}$ to observe the LC alignment properties and electro-optical properties of NP LC cells. LC alignment was characterized in terms of pretilt angle, photomicrograph, and thermal stability of LC molecules. The electro-optical properties monitored were voltage–transmittance (V – T), response time (RT), and residual DC. A negative LC ($T_c = 75^\circ\text{C}$, $\Delta\epsilon = -4$, $\Delta n = 0.777$, MJ98468, Merck Corp.) was injected into the NP LC cells. In addition, to observe the NP structure and chemical affinity of NP surfaces, we performed AFM and contact angle measurements.

3. Results and discussions

In the elastic continuum theory proposed by Berreman,¹ LC molecules align themselves on grooves along the rubbing direction to minimize elastic distortion energies. However, it has also been shown that polymer chains having anisotropic molecular interaction with LCs (such as π – π interaction) are aligned by unidirectional rubbing. As such, the LC alignment theory related to both the surface topography and polymer chain realignment is generally accepted. However, in this study, it is clear that the surface topography is responsible for aligning the LC molecules through the nanoimprint lithography, which does not realign the polymer chains, contrary to the rubbing process.

Fig. 2 shows AFM images of the NP structures transferred to the homeotropic PI layer. The mold pattern is clearly and reliably imprinted into the PI layer as a mirror image. The pitch and

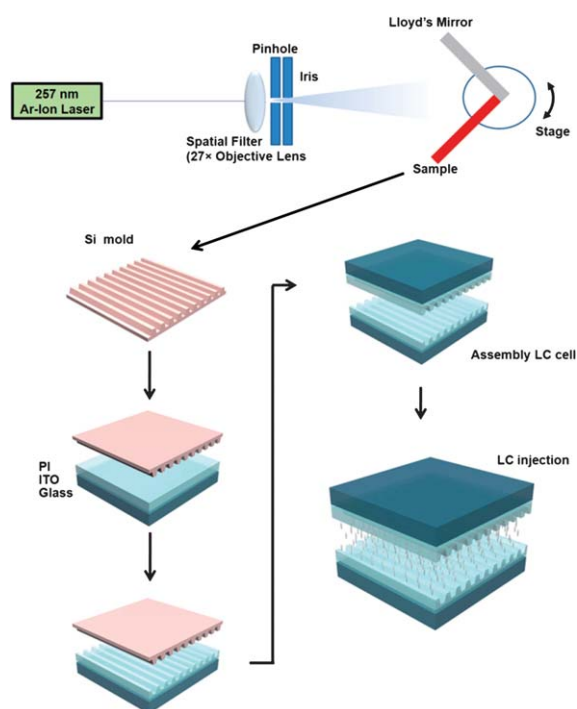


Fig. 1 Schematic illustration of the fabrication of a silicon mold by the LIL process, use of the mold to create replicas of the NP structure in homeotropic PI layers, and implementation of these molded PI layers in the NP LC cell.

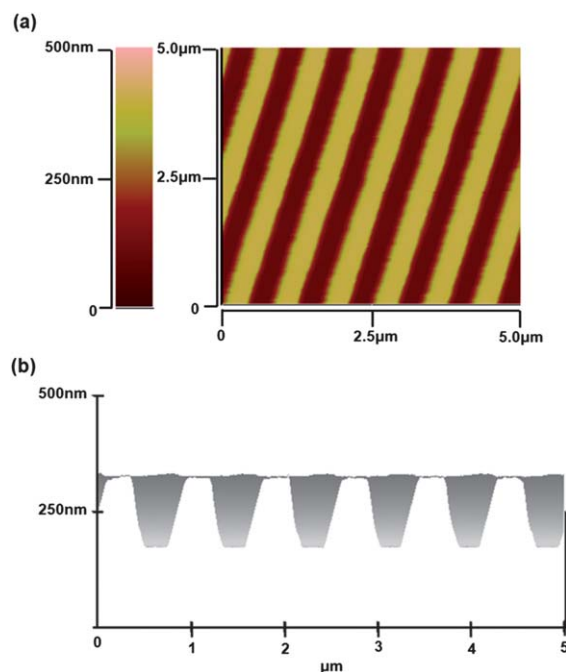


Fig. 2 AFM image: (a) plane view and (b) profile of the imprinted NP surface on the PI layer.

height of the nano-pattern were 380 and 150 nm, respectively, which should be sufficient to align the LC molecules according to the microgroove theory.

Since transparency is the most important factor in the application of nano-pattern substrates to alignment layers, the optical transmittance at 250–800 nm was measured at room temperature using an ultraviolet visible near-infrared scanning spectrophotometer (UV-3101PC, Shimadzu). Fig. 3 shows the measured transmittance of the as-coated PI and NP PI layer on ITO-coated glass substrates. To check for deviations in transmittance we used the transmittance of bare ITO glass as a standard transmittance. Over the wavelength range of 420–780 nm, the average optical transmittances of the bare ITO glass, PI layer, and nano-patterned PI layer were 83.23%, 83.96%, and 77.47%, respectively. About 6.5% of the transmittance loss was observed due to light scattering when light passes through the NP structure. Although the transmittance of the ITO-coated glass with a NP PI layer deteriorated, the difference in the transparency of the bare ITO glass and PI is negligible. Therefore, the transmittance of NP layers on ITO-coated glass is suitable for LCD applications.

Fig. 4 shows transmittance characteristics as a function of the incident angle for measuring pretilt angles of LCs on the NP surface. As can be seen, precise pretilt angle was measured with

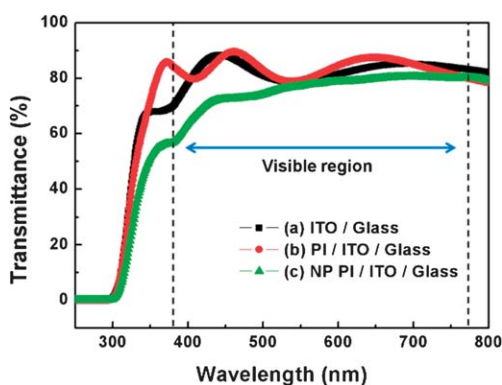


Fig. 3 Optical transmittance spectra of (a) ITO/glass, (b) as-coated PI/ITO/glass, and (c) NP PI/ITO/glass substrates.

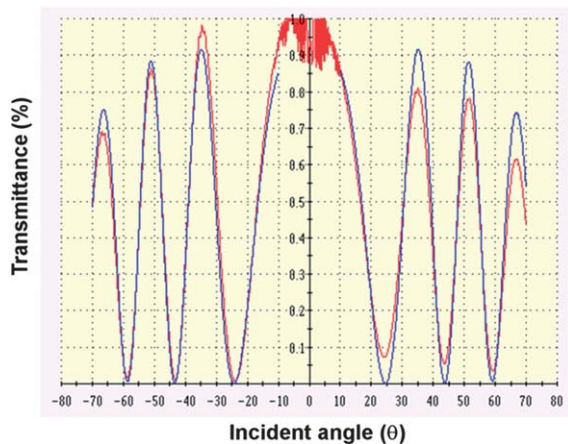


Fig. 4 Transmittance versus incident angle on NP PI layer measured by the crystal rotation method to obtain pretilt angle.

low error, obtained by comparing the experimental graphs (blue lines) with the ideal graphs (red lines) based on simulated information for a given LC, cell gap and birefringence value using a TBA 107 tilt-bias angle evaluation device. Pretilt angle was calculated by the crystal rotation method. The calculated pretilt angle of the LC on the NP surface was 89.8°.

Contact angles and surface energies were also measured to investigate the effect of NP alignment. These parameters can provide an indication of the chemical affinity of the surfaces studied. The contact angle of each surface was measured by the sessile drop technique using a Phoenix 300 surface angle analyzer (SEO), and was further analyzed with IMAGE PRO 300 software. The surface energies were determined from DI-water, glycerol, and diiodomethane according to Young's equation for polar surfaces based on acid–base (van Oss) theory.^{25,26} Table 1 shows the measured contact angles for LC alignment of both as-coated PI and NP surfaces. Contact angles of DI-water, glycerol, and diiodomethane markedly changed when nano-grating patterning was used. Specifically, the hydrophobicity of the PI surface increased with the nano-grating. In previous papers, hydrophobic properties increased proportionally with the contact angle, leading to homeotropic alignment.²⁷ In this work, the change in the chemical affinity of the surfaces is attributed not to realignment of polymer chains but surface topography, inducing uniform alignment of LC molecules. For the as-coated PI layer on ITO glass, LC molecules showed homeotropic orientation. However, when the driving voltage is applied to the LC cells with the as-coated PI layer, LC molecules lie randomly, resulting in poor display quality due to the creation of disclination lines by random alignment.

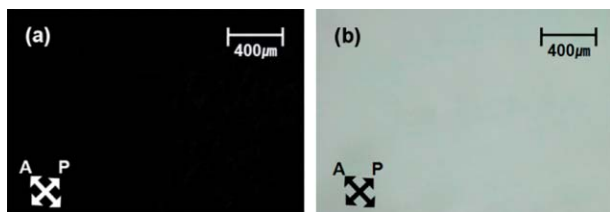
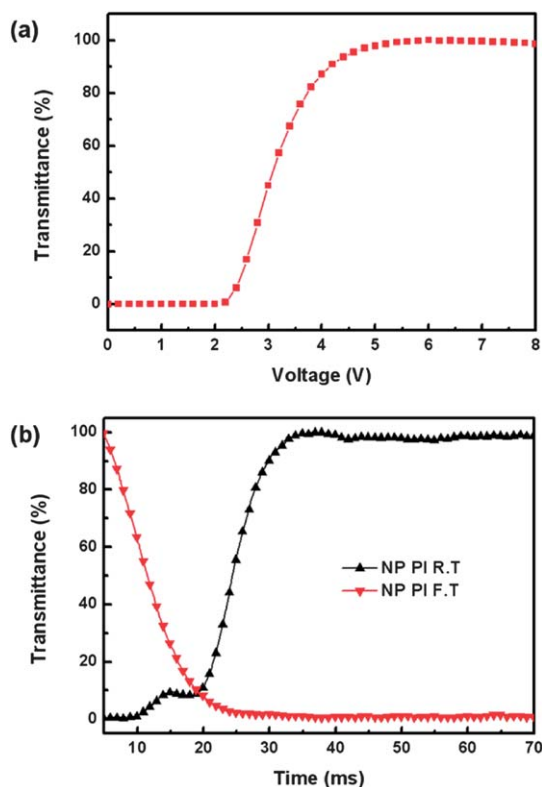
Electro-optical properties were investigated to examine the potential of a nanoimprint technique for LCD applications. Using the NP alignment layer, a VA cell was fabricated. The NP directions on both substrates were parallel to each other, and the cell gap was about 5 μm . The photomicrographs in Fig. 5 show the operations of the NP LC cell between crossed polarizers. In the off state, LC molecules remain perpendicular to the NP surface and the light transmission is prohibited, resulting in a dark image. When the electrical field is applied to the cell (on state), LC molecules shift to a horizontal position, parallel to the NP surface, and the NP LC cell clearly transmits visible light generated from backlight units, resulting in a white image. This indicates that uniform alignment was achieved for the NP LC cell.

Fig. 6 shows the V - T , RT curves when a driving voltage was applied to the NP LC cell. As shown in Fig. 6(a), a V - T curve with no optical bounce effect was obtained. The threshold voltage of the NP LC cell was 2.472. Fig. 6(b) shows the RT characteristics. The NP LC cell exhibited comparable performance in this respect with a rise time of 10.2 ms and a fall time of 12.5 ms.

Image sticking is also a very important factor in the operation of LCDs. Therefore, we measured the residual DC by the voltage-dependent capacitance, as shown in Fig. 7. The DC voltage was swept from 0 to +5 V, and then was changed from +5 to -5 V, and finally from -5 to 0 V, with a step size of 0.1 V. Amplitudes of the residual DC at positive and negative cycles, which are defined as the voltage difference between the rise and fall at half of the maximum capacitance, were 0.144 and 0.132 V,

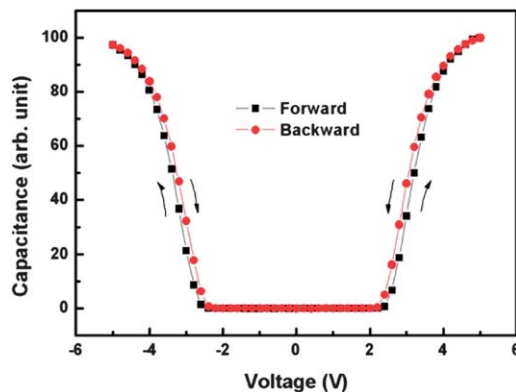
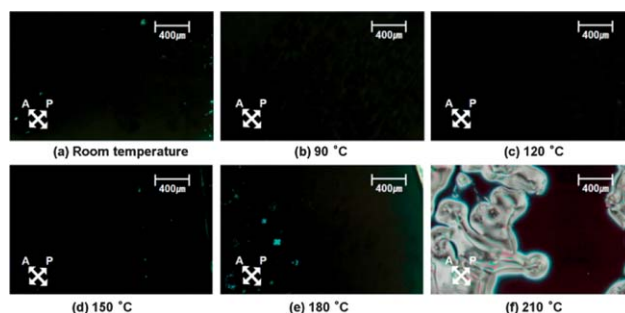
Table 1 Values of contact angles measured for DI water, glycerol, and diiodomethane and the surface energies of as-coated PI and NP PI surfaces

Sample	$\Theta_{\text{water}}/\text{deg}$	$\Theta_{\text{glycerol}}/\text{deg}$	$\Theta_{\text{diiodomethane}}/\text{deg}$	$\gamma_s^d/\text{mJ m}^{-2}$	$\gamma_s^p/\text{mJ m}^{-2}$	$\gamma_s = \gamma_s^d + \gamma_s^p$
V-PI	90.30 ± 0.2	77.41 ± 0.4	33.43 ± 0.2	42.743	-0.894	41.850
VP-PI	99.36 ± 0.2	102.33 ± 0.5	37.45 ± 0.3	40.825	-10.682	30.144

**Fig. 5** Optical photomicrographs of the LC molecules on NP PI surface under crossed Nicols: (a) off-state with no applied voltage and (b) on-state with applied voltage of 5 V.**Fig. 6** (a) V - T and (b) RT curves of the NP LC cell (R.T.: rise time, F.T.: fall time).

respectively. The residual DC method is the same as used by Nissan chemical, wherein the electrical capacity of the LC panel is measured from the gap in the C - V hysteresis.

Fig. 8 shows the photomicrographs of the NP LC cell that were taken to examine the relationship between the ability of the LC molecules to maintain their orientation and thermal stability. Before the annealing process, NP LC cell was clear without any defects such as disclinations or debris spots. The NP LC cells were annealed from 0 to 210 °C for 10 min to examine the

**Fig. 7** Measured hysteresis curve in voltage-dependent capacitance of the NP LC cell.**Fig. 8** Photomicrographs of NP LC cell annealed at (a) room temperature, (b) 90, (c) 120, (d) 150, (e) 180, and (f) 210 °C, respectively to examine thermal stability.

thermal stability of the NP LC cells. Fig. 8(a)–(e) show photomicrographs obtained after annealing from 0 to 180 °C, respectively. The LC molecules maintained uniformly stable alignment, but, in Fig. 8(f) for 210 °C, unstable and partially aligned LCs in the cracking state were observed. These results indicate that LC molecules on NP surfaces have high thermal budget, which could be advantageous for the development of LCDs.

4. Conclusion

In summary, this paper demonstrates several aspects of nanoimprint lithography and its use in the field of LCDs. Deep-ultraviolet LIL was applied for the first time to fabricate a NP structure. The LIL process is more convenient and economical than any other process for the fabrication of nanostructures. Transmittance measurements on the NP layer on ITO coated glass showed that the transparency is sufficient for LCD applications. Further, NP LC cells were fabricated which showed a performance competitive with conventional LC cells. Uniform LC alignment was achieved on the NP LC cell. The hydrophobic

behavior of the NP PI surface was shown by contact angle measurements, which revealed LC molecules homeotropically aligned by surface topography. Electro-optical properties including $V-T$ and RT of NP LC cell were comparable to that of a rubbed PI cell. Therefore, this proposed approach is expected to be applicable as an alternative to the conventional rubbing process for LC alignment.

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