Anisotropic Nano-Imprinting Technique for Fabricating a Patterned Optical Film of a Liquid Crystalline Polymer

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We developed an anisotropic nano-imprinting technique, which combines the exposure of ultraviolet light, to fabricate a patterned optical film of a liquid crystalline polymer (LCP). The nano-imprinted LCP film has two-fold functionality of an in-cell retarder and an alignment layer of liquid crystal (LC) molecules. In addition to the geometrically generated microgrooves, the anisotropic surface interactions of the LCP acquired at a nano-scale level during the imprinting process results in the LC alignment on the patterned LCP film without any surface treatment. The nano-imprinted, quarter wave LCP was implemented into a LC cell which produces half-wave retardation under crossed polarizers.

Keywords: Nano-Imprinting, Liquid Crystal (LC), Liquid Crystalline Polymer (LCP), Patterned Optical Film, In-Cell Retarder.

1. INTRODUCTION

In recent years, organic electro-optical materials have great interest for applications in optical components, LC displays and biomedical devices. Among them, liquid crystalline polymer (LCP) materials are one of the classes that have been widely used for optical retarders,\(^1\), color filters,\(^2\) polarization converters\(^3\) and interference filters.\(^5\) In such cases, it is necessary to produce the LCP into an optically anisotropic film structure. For aligning the LCP molecules, a rubbed surface\(^6\) or a photo-treated surfaces\(^2\) have been used previously. However, the rubbing process inevitably involves the mechanical damage and dust particles on the alignment surface and the photoalignment suffers from the weak anchorage of the LCP on the photo-treated surface.\(^7\) Moreover, a baking process of an alignment layer at a high temperature over 120 °C is required. Therefore, a new technique which is capable of aligning the LCP molecules and patterning the LCP film at a low temperature needs to be developed for fabricating organic-based microstructure devices.

In this work, we developed a novel nano-imprinting technique, based on a lithography,\(^8\)\(^,\)\(^9\) in combination with the exposure of ultraviolet (UV) light to produce a wide range of anisotropic optical films of the LCP. It is extremely important to produce a patterned LCP film which can be used as both an in-cell retarder and an alignment layer for next-generation LC displays. The anisotropic surface forces of the LCP produced at a nano-scale level during the imprinting process result in the LC alignment on the patterned LCP film without any surface treatment. The anisotropic LCP film with chain ordering by nano-imprinting was implemented into a LC cell to serve as an alignment layer of the LC as well as an in-cell retarder.

2. EXPERIMENTAL DETAILS

2.1. Fabrication of a Polymer (PDMS) Mold

The master made of a UV curable photopolymer material (NOA63, Norland Ltd.) was used to fabricate a polymer mold. We used a poly(dimethylsiloxane) (PDMS, GE silicons) as a polymer mold with micro-patterns. As shown as Figure 1(a), the PDMS was first poured on the master to give the polymer mold with thickness of 5 cm. It was then cured on a hot plate at about 70 °C, at which the adhesion between the PDMS mold and the master is relatively small, for 5 hours. The PDMS mold was finally peeled off from the master. The period of the PDMS mold was varied from 3.0 to 8.0 \(\mu m\) with the line-to-space (LS) ratio from 0.5 to 2.0, and the depth was fixed as 1.2 \(\mu m\). The feature sizes were determined by using a scanning electron microscopy (SEM).

2.2. Imprinting Technique for Fabricating a Patterned LCP Film

We used a commercial LCP material, RMS 03-001 (Merck), to fabricate an anisotropic optical film.
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Figure 1(b) shows a schematic diagram of producing a patterned LCP film through a nano-imprinting process which utilizes our PDMS mold. The LCP material was spin-coated on a glass substrate at the spinning rate of 2500 rpm for 30 seconds without a pre-coated alignment layer, giving the layer thickness of 1.5 μm, and baked subsequently at 65 °C for 1 minute. By pressing the PDMS mold onto the prepared LCP layer, micro-patterns of the mold were replicated on the LCP layer. The micro-patterns of the PDMS mold were well transferred to the surface of the LCP layer under an imprinting pressure resulting from just above a gravitational force of the PDMS mold. After the micro-patterns were formed on the LCP layer, the LCP layer was exposed to the UV light at the intensity of 40 mW/cm² for 5 minutes under a nitrogen atmosphere so as to preserve the shapes of the micro-patterns. The patterned LCP film was then peeled off from the PDMS mold. The optical anisotropy was observed with a polarizing optical microscopy (POM, Optiphot2-Pol, Nikon) and the phase retardation was measured using a photo-elastic modulation (PEM) method.

2.3. The LC Alignment on a Patterned LCP Film

Using the Berreman concept, microgrooves were prepared on the LCP film to explore the possibility of aligning the LC molecules without using any surface treatment or an extra alignment layer. A nano-imprinted, patterned LCP film was implemented into a LC cell to examine two-fold functionality of an alignment layer and an in-cell phase retarder. Our LC cell have a patterned quarter-wave plate (QWP) LCP film on the lower glass substrate and a polyimide (PI) alignment layer of JALS 146-R50 (JSR co., Japan) on the upper glass substrate for the planar LC alignment. The LC cell was placed between crossed polarizers such that one of the optic axes was at 45° with respect to the direction of the rubbing direction on the PI layer. The cell thickness was maintained 3.2 μm thickness using glass spacers so that the LC layer corresponds to the QWP. The LC material used was MLC-6012 (Merck) and injected into the cell by capillary action at room temperature.

3. RESULTS AND DISCUSSION

3.1. Microstructures Imprinted on the LCP

Figure 2 shows the SEM images of microstructures produced on various PDMS molds and those transferred on the LCP films from the PDMS molds. The SEM images shown from Figures 2(a to d) correspond to the patterns having the periods of 3.0 μm with the LS ratio of 0.5, 3.0 μm with the LS ratio of 1.0, 8.0 μm with the LS ratio of 1.0, and 3.0 μm with the LS ratio of 2.0. The depth of the mold patterns was about 1.2 μm. Figures 2(e–h) show the SEM images of the nano-imprinted LCP films, corresponding to the negative line shapes of the PDMS molds, whose periods are 3.0 μm with the LS ratio of 2.0, 3.0 μm with the LS ratio of 1.0, 8.0 μm with the LS ratio of 1.0, and 3.0 μm with the LS ratio of 0.5, respectively. Note that the PDMS mold has sufficient rigidity to prevent the collapse of microstructures, and at the same time, it is soft enough to release the LCP film. Using our nano-imprinting process combined with the UV exposure, micro-scale lines will be patterned with high regularity at...
precisely determined micro-scale intervals, strongly indicating that microstructures can be patterned with high feature density and precision. As shown in Figures 3(a and b) that are the field emission SEM (FESEM) images of the patterned LCP surfaces, the nano-size broken defects and damages indicated by red arrows are sometimes observed depending on the processing temperature and the surface conditions. Those defects seem to appear when the feature size, the rigidity, and the adhesion strength of the PDMS mold are not properly selected. More importantly, the surface contamination of the PDMS mold is likely to produce structural defects shown in Figures 3(a and b). However, in the range of the visible wavelength, the nano-size defects on the imprinted LCP film have no appreciable effect on the optical properties as long as the depth of each mold pattern is still maintained (in this case, about 1.2 μm).

### 3.2. The Imprinted LCP Film as an In-Cell Phase Retarder

Figure 4 shows microscopic textures of our imprinted LCP films, observed with the POM under crossed polarizers, having different pattern sizes of 3.0 μm and 8.0 μm in period and the LS ratio from 0.5 to 2. The depth of each mold pattern is about 1.2 μm. The dotted lines represent the boundaries between the imprinted region with patterns and the bare region with no patterns. The direction of the mold patterns on the imprinted LCP film is parallel (0°) to the optic axis of the polarizer or that of the analyzer in Figures 4(a–d) while it makes an angle of either 45° or 135° to the optic axis of the polarizer in Figures 4(e–h). The microscopic textures from Figures 4(a to d) [or from Figs. 4(e to h)] correspond to the patterns having the periods of 3.0 μm with the LS ratio of 2, 3.0 μm with the LS ratio of 1.0, and 3.0 μm with the LS ratio of 0.5. Except for the period of 8.0 μm as shown Figure 4(g), all the cases of 3.0 μm in period show a completely bright state when the direction of the mold patterns makes an angle of either 45° or 135° to the optic axis of the polarizer. The insufficient phase retardation as the QWP in Figure 4(g) indicates that the LCP molecules did not fully aligned at a nano-scale level during the imprinting process.

We now describe the phase retardation of an imprinted LCP film itself and that of the LC cell with an in-cell LCP film to examine the two-fold functionality of the imprinted LCP film as an alignment layer and an in-cell QWP. Figure 5(a) shows the schematic diagram of our LC cell configuration where the LC layer behaves as another QWP. The planar alignment of the LC molecules along the direction parallel to the microgrooves was obtained on the imprinted LCP film similar to the imprinted polymer.
layer with microstructures.\textsuperscript{13} As shown in Figure 5(b), the phase retardation of $\pi/2$ through the imprinted LCP film itself, measured using the PEM method as a function of the azimuthal rotation angle at the wavelength of 632.8 nm, corresponds exactly to the QWP. The measured phase retardation of $\pi$ through our LC cell with the in-cell LCP film behaving as a QWP tells us that the LC molecules were well aligned on the imprinted, in-cell LCP film and the LC layer alone produces the phase retardation of $\pi/2$. The total phase retardation through the LC layer and the in-cell LCP film corresponds to the half-wave plate. The electro-optic properties of the LC cell in Figure 5(a), adapting the imprinted LCP, were well preserved over several months. The electro-optic properties of the LC cell in Figure 5(a), adapting the imprinted LCP, were well preserved over several months. The electro-optic properties of the LC cell in Figure 5(a), adapting the imprinted LCP, were well preserved over several months. It is expected that the use of a patterned in-cell retarder such as our imprinted LCP film allows for high transmission, no parallax, and wide viewing characteristics in a variety of the LC-based optical devices.

4. CONCLUSION

We developed an anisotropic nano-imprinting technique, combined with the exposure of UV light, to produce a patterned optical film of a LCP material. The patterned LCP film can be used as both an in-cell phase retarder and an alignment layer of the LC for the LC-based optical devices. The magnitude of the orientational order of the LCP molecules, acquired at a nano-scale level during the imprinting process, depends on the feature size, the adhesion, and the surface properties of the PDMS mold. A new type of the LC cell with an in-cell LCP film as a QWP was demonstrated in this work. The imprinting technique presented here provides a fast, low-cost process for the parallel replication of two-dimensional microstructures of a LCP material where anisotropic surface interactions would be tailored at a nano-scale level.

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References and Notes

10. Datasheet provided by E. Merck Company.

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