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Influence of Rapid Thermal Annealing on Molecular Orientation of Planar Cholesteric Liquid Crystal

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Rapid thermal annealing enables removal of orientation defects in planar cholesteric liquid crystal (CLC). We investigate influence of rapid annealing and cooling on molecular orientation in CLC. Annealing temperature strongly affects the number of treatment cycles required for improved orientation, and an effective annealing temperature range is very narrow. Both annealing and cooling are effective for removal of orientation defect in planar CLC. The number of the treatment cycles depends on viscosity of CLC. The rapid thermal processing is applicable to chiral dopants having various thermal properties.

Keywords: colesteric liquid crystal; molecular orientation; rapid annealing; rapid cooling; rapid thermal processing

I. INTRODUCTION

Cholesteric liquid crystals (CLCs) have a nanohelical structure formed by self-assembly. CLCs have recently attracted much attention because they can be regarded as a one-dimensional pseudophotonic crystal [1–5]. Photonic crystals consisting of dielectric periodic structures with an interval of submicron length have photonic band gaps [6,7]. Using this novel concept, photonic crystals enable the development of next-generation optical devices such as low-threshold lasers and microoptical circuits. Unfortunately, the fabrication of periodic structures with a periodicity equivalent to the visible wavelength requires a high-cost process. Therefore, a self-assembling

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CLC with nanohelical structure would be advantageous for nanostructure fabrication.

The uniformity of molecular orientation is a key factor in the quality of liquid crystal applications. Orientation technology of CLCs is of considerable importance not only for photonic crystal applications but also for fundamental research. In general, an increase in cell thickness causes a decrease in the order parameter of a CLC. The reason for this is that the orientation force is only due to a polyimide film on the glass surface and its effect decreases with increasing cell thickness. Recently, we proposed an orientation method for CLCs using acoustic streaming [8,9]. Using this method, CLC molecules are reoriented from multi-domain focal conic state to a planar state by molecular flow.

More recently, we discovered an easier method of improving the orientation of a planar CLC by rapid thermal processing (RTP) [10]. This RTP technique enables removal of defect in planar CLC in a thick cell. In semiconductor fabrication process, RTP has been studied for improvement in crystalline quality [11]. In contrast, there are several studies of RTP for CLC [12–15]. To our knowledge, improvement in CLC molecular orientation using RTP has not been investigated in detail. In this paper, we investigate molecular reorientation of CLC using rapid annealing and cooling conditions. We also attempt to remove orientation defects in CLCs having different thermal properties. Finally, a uniform planar CLC cell with thickness over 100 μm is achieved using the method.

II. EXPERIMETNAL PROCEDURE

A CLC was obtained by mixing a nematic liquid crystal (E44, Merck) and a chiral dopant (MLC6247, Merck) of 26 wt%. The pitch length of the CLC was approximately 360 nm at 27°C. The cholesteric-isotropic transition temperature was around 91°C. We prepared a typical sandwich cell using two glass substrates and poly(ethylene terephthalate) films. To obtain a planar orientation, the inner surfaces of the cell were coated with polyimide (AL1254, JSR) and were rubbed unidirectionally. The rubbing conditions were as follows: the rotation speed of the roller was 500 rpm, the rubbing depth was 0.5 mm, the speed of the stage was 0.6 cm/s, and the rubbing process was repeated 10 times. The CLC was filled in the cell at the isotropic phase, and was then slowly cooled to room temperature (RT) at a rate of −0.5°C/min. Using this method, a uniform planar orientation can be obtained in a thin cell. However, many defect lines appear in a thick cell. For example, it is difficult to obtain a uniform planar orientation in a 50-μm-thick cell by this conventional method.

We attempted to improve the orientation of planar CLCs in a thick cell by RTP, which was performed from several degrees below the cholesteric-isotropic transition temperature down to RT. That is, the sample was annealed at the temperature using a temperature bath, and then was cooled to RT by exposing it to air. One cycle of RTP involved rapid annealing followed by rapid cooling. The temperature was controlled using a temperature controller (FP82, Mettler). This RTP was repeated until the multi-domain focal conic state changed to a planar state. To observe orientation change, the microscopic and overall images of the sample were taken after each repetition. The transmission spectrum of the sample also was measured after each repetition.

III. RESULTS AND DISCUSSION

Figure 1 shows microscopic images of CLC orientation changes in a 50-μm-thick cell by RTP. The triangular shadow on the bottom-right corner was used as a marker for observing the same area in the cell. As shown in Figure 1(a), we obtained a multi-domain focal conic state as an initial orientation by filling CLC at the isotropic phase and slow cooling. In spite of the surface being coated with polyimide and rubbed unidirectionally, the CLC did not have a planar orientation but a multi-domain focal conic state. Here, the sample was annealed at 91°C for 18 s using a temperature bath, and then was cooled to RT

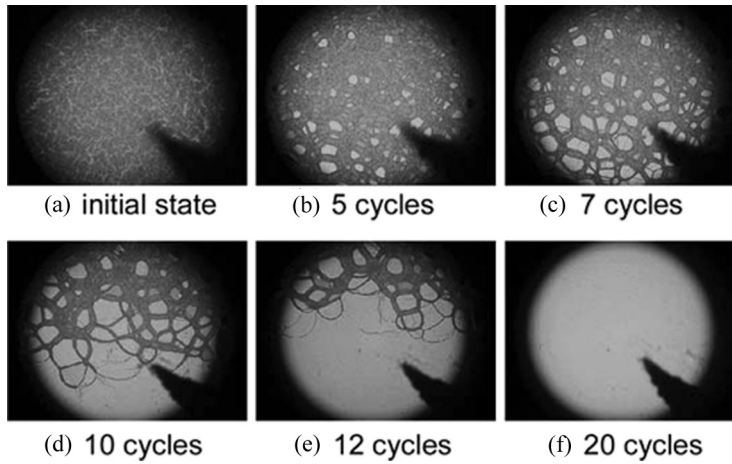

FIGURE 1 Microscopic images of CLC reoriented by rapid thermal processing (RTP).

in 2 min by exposing it to air. Figure 1(b) shows the texture of the CLC after 5 cycles of RTP, where one cycle involves rapid annealing followed by rapid cooling. Note that small planar domains appear at several locations within the CLC. After 10 cycles, the planar domains enlarged gradually and the amount of the focal conic state decreased. We obtained a uniform planar CLC after 20 cycles, as shown in Figure 1(f).

Overall views of the initial and RTP treated cells are shown in Figure 2. Figures 2(a) to 2(f) correspond to the overall views of the cell shown in Figures 1(a) and 1(f), respectively. The initial CLC shown in Figure 2(a) was opaque due to scattering, and the background letters could not be recognized. After 5 cycles of RTP, the orientation defects decreased as shown in Figure 2(b). The orientation defects gradually decreased with increasing RTP cycle. Finally, we could easily recognize the letters behind the treated cell shown in Figure 2(f). The results indicated that the RTP induced planar orientation in the CLC.

Figure 3 shows the transmission spectra of the sample before and after RTP. Before RTP, the band edges of the stop band were broad, and the maximum transmittance was less than 40% owing to light scattering. After 20 cycles of RTP, we obtained a uniform planar orientation in CLC. Although 20% or less scattering was observed, the spectra exhibited higher transmittance and the stop band edges became sharp.

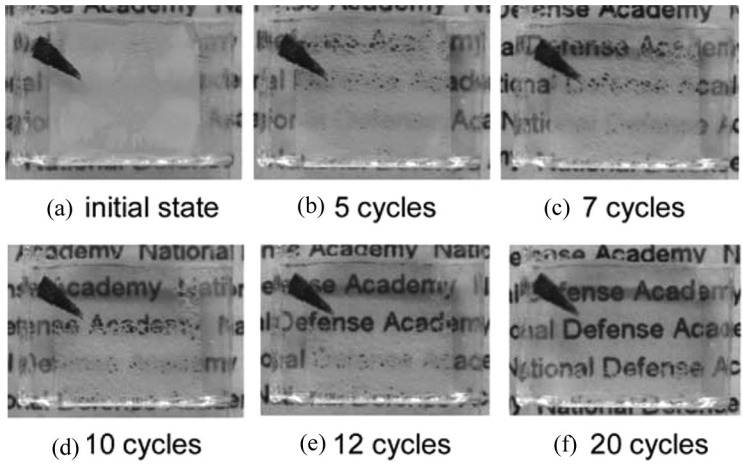

FIGURE 2 Overall views of initial cell and treated cells. These pictures correspond with the overall views of the microscopic images in Figures 1(a) to 1(f).

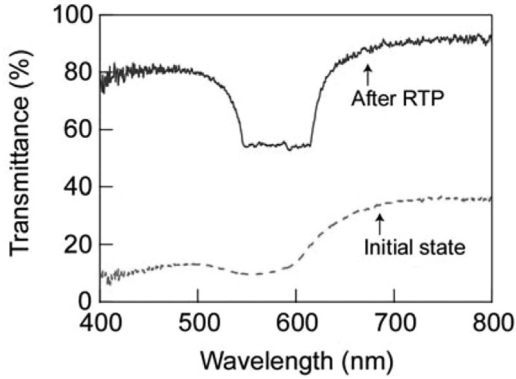

FIGURE 3 Transmission spectra of initial cell and cell after 20 cycles of RTP.

We also investigated the annealing temperature dependence of the number of cycles required to obtain a uniform planar CLC. The annealing temperatures were set to 86, 88, 89, and 91°C. To accurately investigate an optimal temperature, the annealing time was elongated from 18 s to 2 min. That is, the sample was annealed at each temperature for 2 min, and then was cooled to RT in 2 min by exposing it to air. In this examination, we reused a sample after reset molecular orientation using rapid cooling from isotropic temperature. Before this examination, we confirmed that reuse of one sample did not influence this CLC reorientation examination. The photographs of the cell after RTP with the different annealing temperatures are shown in Figure 4. It is evident that the reorientation of the CLC is affected by the annealing temperature. Annealing at 88°C induces a uniform planar orientation after 10 cycles. In contrast, annealing at 86 and 89°C improves orientation segmentally after 10 cycles, but focal conic domains still remain. On the other hand, by polarizing microscopy, we observed that isotropic domains appeared partially within the CLC above 89°C. After annealing at 91°C for 2 min, a complete phase transition occurred in the sample. Therefore, 91°C annealing did not induce an orientation change from the focal conic state to the planar state. This indicated that the molecular orientation was reset at the isotropic phase. The previous examination shown in Figures 1–3, we were able to obtain a good orientation using 91°C annealing. This is because the annealing time of 18 s is shorter than that of this examination. We consider that a complete phase transition did not occurred using the shorter annealing. The important points here are that the number of treatment cycles strongly depends on the

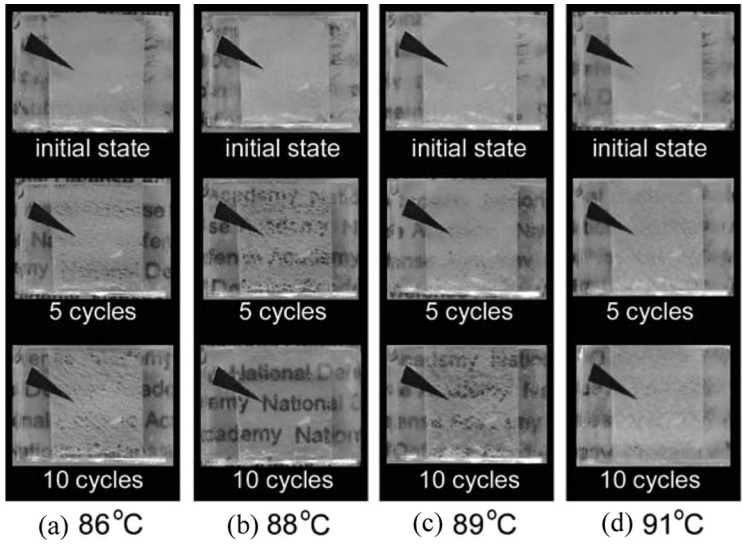

FIGURE 4 Photographs of CLC cells after RTP with the different annealing temperatures of (a) 86°C, (b) 88°C, (c) 89°C, and (d) 91°C.

annealing temperature and the optimal CLC orientation occurs at the upper-limit temperature of the cholesteric phase.

After annealing temperature examination, I had a question whether the important factor was rapid annealing or rapid cooling. We also examined reorientation in CLC by rapid annealing or rapid cooling. In rapid annealing examination, the sample was quickly annealed at 88°C for 2 min, and then was slowly cooled to RT at a rate of −0.5°C/min. In rapid cooling, the sample set in temperature bath, and then annealing temperature gradually increased to 88°C at a rate of 0.5°C/min. After temperature became 88°C, the sample was quickly cooled to RT in 2 min by exposing it to air. Figure 5 shows

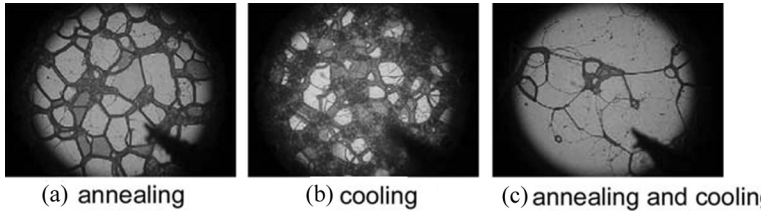

FIGURE 5 Microscopy images after 10 cycles of three different treatments: (a) rapid annealing, (b) rapid cooling, and (c) rapid annealing and cooling.

the microscopy images after 10 cycles of three different treatments. Note that both annealing and cooling are effective for removal of orientation defect in the planar CLC. Therefore, the combination of annealing and cooling showed the best orientation in the three treatments. In addition, the reorientation was occurred when the helix of CLC elongates or shortens. This indicates this RTP method does not depend on the thermal characteristic of chiral dopant.

We investigated reorientation in the CLC mixed with another chiral dopant (S811, Merck) having a different thermal property. The same nematic mixture E44 was used as the host material, and the concentration of S811 was 30 wt%. The cholesteric-isotropic transition temperature of the CLC including S811 was 67°C. The pitch of the S811-doped CLC shortened with increasing temperature, whereas that of the MLC6247-doped CLC lengthened with increasing temperature. Figures 6(a) and 6(b) show the transmission spectra of the MLC6247- and S811-doped CLCs at their initial states, respectively. The thicknesses of both cells were 50 μm. It can be easily confirmed that the stop bands of the MLC6247- and S811-doped CLCs shift to longer and shorter wavelengths with increasing temperature, respectively. Before RTP, the band edges of the stop band were broad, and the maximum transmittance was about 40% owing to light scattering. After 30 cycles of RTP, we obtained a uniform planar orientation in both CLCs. The transmission spectra of the MLC6247- and S811-doped CLCs after treatment are shown in Figures 6(c) and 6(d),

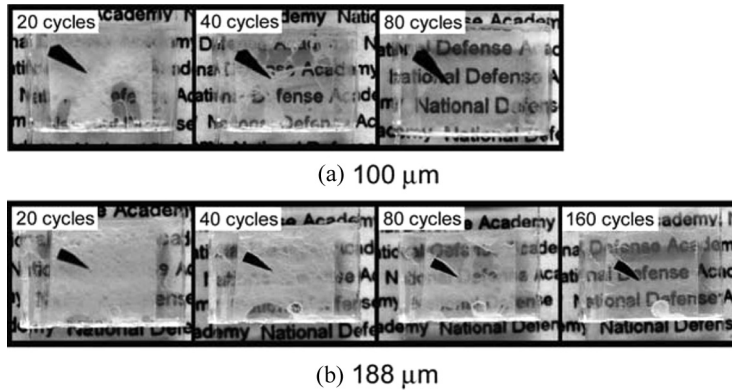

FIGURE 6 Transmission spectra at various temperatures: (a) initial cell of MLC6247-doped CLC, (b) initial cell of S811-doped CLC, (c) cell of MLC6247-doped CLC after 30 cycles of treatment, and (d) cell of S811-doped CLC after 30 cycles.

respectively. The annealing time was 18 s and the cooling time was 2 min. The annealing temperatures of the MLC6247- and S811-doped CLCs were 91 and 65°C, respectively. Although 20% or less scattering was observed, the spectra exhibited higher transmittance and the stop band edges became sharp. These results confirmed the RTP method did not depend on the thermal characteristic of chiral dopant.

We also examined reorientation in the CLC mixed with another host material (BL011, Merck). The chiral dopant of MLC6247 was used at a concentration of 25.5 wt%. The cholesteric-isotropic transition temperature of this sample was around 59°C. We prepared a 500-μm-thick cell as the same manner as the above exams. The sample was annealed at 55°C for 40 s, and then was cooled to RT in 2 min by exposing it to air. Figures 7(a)–(c) show the microscopy images of initial state, after 40 cycles, and after 100 cycles, respectively. We were able to obtain a good planar CLC after 100 cycles. This sample required large number of RTP cycles. This is because the viscosity of BL011 is higher than that of E44. This indicates the RTP cycle number depends on the molecular mobility of sample.

To explain the behavior of multi-domain focal conic domain reduction, the following mechanism is proposed. The rapid annealing leads to a temperature difference between the surface and inside the CLC; the temperature in the vicinity of the surface increases rapidly, whereas the temperature inside the CLC increases gradually. This induces different rates of thermal expansion in the CLC layer, which produces thermal stress in the CLC. The rapid cooling also produces thermal stress due to the opposite temperature difference. We consider that these thermal stresses cause the disappearance of domain walls in the CLC. In addition, because the increase in temperature leads to a decrease in viscosity, the molecular mobility of

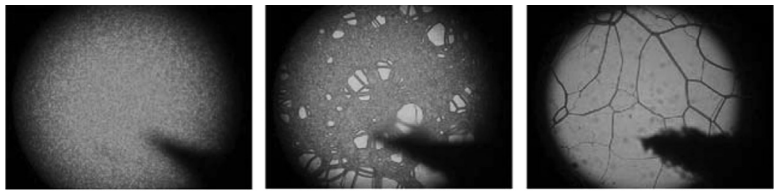

FIGURE 7 Microscopic images of CLC mixed with nematic liquid crystal of BL011 and chiral dopant of MLC6247: (a) initial state, (b) after 40 cycles of treatment, and (c) after 100 cycles.

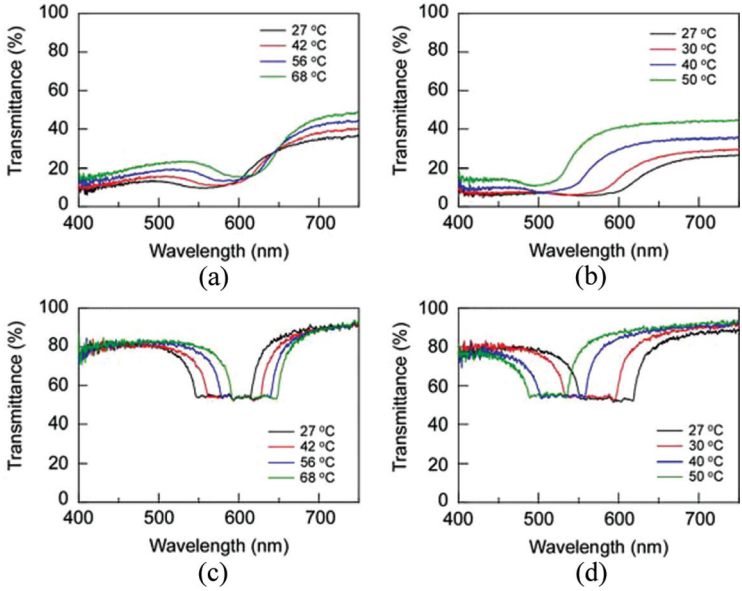

FIGURE 8 Molecular orientation changes of (a) 100 and (b) 188-μm-thick cells treated by rapid annealing at 91°C and rapid cooling to RT.

the CLC increases with temperature. In particular, the molecular mobility is higher near the cholesteric-isotropic transition temperature. Therefore, we consider that the increase in mobility accelerates the relaxation of domain walls in the CLC.

Finally, we attempted to reorient molecules in 100 and 188-μm-thick CLC cells. Figure 8 shows the orientation changes in these cells. The annealing and cooling temperatures were 91°C and RT, respectively. As is evident from Figure 8, the focal conic domains in both cells change to the planar orientation. The 100-μm-thick cell required more treatment cycles than the 50-μm-thick cell. Thus, we found that the number of cycles required to obtain a planar orientation increased with increasing thickness. In the 188-μm-thick cell, although some small defects were observed using a microscope, we could obtain a planar orientation after 160 cycles.

IV. CONCLUSION

We demonstrated CLC molecular reorientation from multi-domain focal conic state to planar state by RTP. The annealing temperature

strongly affected the number of treatment cycles required for reorientation and the effective annealing temperature range was very narrow. Examination of rapid annealing or rapid cooling showed that both annealing and cooling were effective for removal of orientation defect in planar CLC. Therefore, the combination of annealing and cooling showed the best orientation in the three treatments. This indicated this RTP method did not depend on the thermal characteristic of chiral dopant. In fact, this method was applicable to chiral dopants having various thermal properties. In the treated cell, scattering was reduced and sharp band edges appeared in the transmission spectra. Furthermore, a uniform planar orientation in a 188-μm-thick cell was obtained using this method. We believe that this orientation method is useful for fundamental research and applications using CLCs.

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