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Alignment characteristics of nematic liquid crystals on micro-scale grating structures fabricated by direct laser writing employing two photon excitation has been investigated upon changing periods and heights of the grating. Liquid crystal was infiltrated in the cell made of a substrate with gratings and another glass substrate with polyimide rubbed in the direction almost parallel to the grating vector of the structure in order to realize a twisted nematic configuration. Anchoring energies of the gratings were evaluated using the torque balance method, and were confirmed to be proportional to the height and inversely to the period of the grating.

While the anchoring energy of the gratings turned out to be weaker compared to substrates treated by the conventional rubbing method, varying periods and heights of the grating allowed control of the anchoring energy.

Keywords Direct laser writing; nematic liquid crystal anchoring; torque balance method

Introduction

Alignment of liquid crystal (LC) molecules is one of the most important factors that determine the performance and function abilities of LC devices. Generally, large surface area alignment of the LC is achieved by rubbing on the polymer surface. However, it is not suitable for local alignment control in arbitrarily patterned regions. Recently, precise alignment control in micro-domains has attracted attention from a point of view of creating novel functionalities.

Locally rubbing the surface of a polymer using the stylus of an atomic force microscope (AFM nano-rubbing) [1,2] has been demonstrated as one of the local alignment methods. Using the exquisite technique, bistable and tristable orientational switching of nematic LC (NLC) was achieved.

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We have proposed local area alignment of NLC on micro-grating structures fabricated by curing an ultraviolet curable material using a two-photon excitation laser-lithography process [3]. By directly scanning a focused laser spot on the sample, arbitrarily patterned structures can be designed with ease. Especially, focusing tightly a femto-second laser beam causes two photons to contribute to the reaction concurrently in the vicinity of the focus point, which makes it possible to realize a pinpoint photo-polymerization and to fabricate miniature structures with high resolution beyond the diffraction limit. In this study, a detailed study on the LC alignment characteristics on the grating structures fabricated by two photon excitation direct laser writing (TPE-DLW) is reported.

Experimental

The light-curing material used in the micro-grating fabrication process comprised of a colorless, urethane-based ultraviolet (UV)-curable photopolymer (Norland: NOA 61), with 0.1 wt% of bis(2,4,6-trimethylbenzoy) phenylphosphine oxide (Ciba: Irgacure 819) to enhance an absorption at $\lambda = 400$ nm and 0.1 wt% of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (Exciton: DCM) dye for observation purposes. NOA 61 was chosen due to its fast curing time, good adhesion and chemical stability. The NLC material used to demonstrate alignment properties was 4-n-pentyl-4′-cyanobiphenyl (Merck: 5CB) ($n_o = 1.522$, $n_e = 1.706$).

An experimental setup for the fabrication process is schematically illustrated in Figure 1. Experiments were performed under dark conditions to avoid unnecessary curing of the material. TPE-DLW was performed using a confocal laser scanning microscope (CLSM) system (Carl Zeiss: LSM 510). A target cover glass with the spin-coated curable photopolymer was mounted on the stage of the CLSM and irradiated with 100 fs pulses of a focused Ti:sapphire laser (Spectra Physics: Maitai) at $\lambda = 800$ nm and repetition rate of 80 MHz. The laser beam was focused by a high numerical aperture oil-immersion objective lens (63x, N.A = 1.4) and the position of a focused spot was controlled by a galvanometer to scan arbitrarily within a maximum scanning area of $146.2 \times 146.2\,\mu m^2$. The material within the designated region was cured with a single scan. The uncured material was removed by rinsing in acetone for 20 s and ethanol for 30 s, so that the cover glass surface was left only with the cured micro-grating structure. We confirmed the fabricated micro-grating structure under an AFM (JEOL: JSPM-4210). The grating of the sample was 520 nm. The AFM image is shown in Figure 2(a), and Figure 2(b) shows height profile along line AB is shown in Figure 2(a).

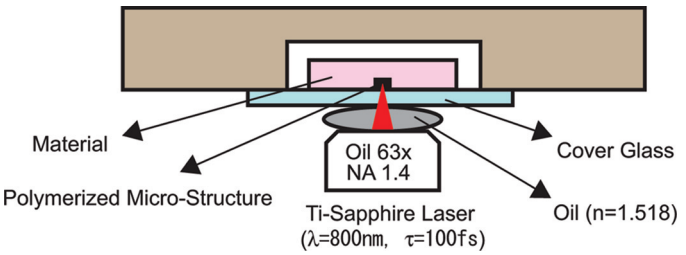

Figure 1. Schematic diagram of the experimental setup.

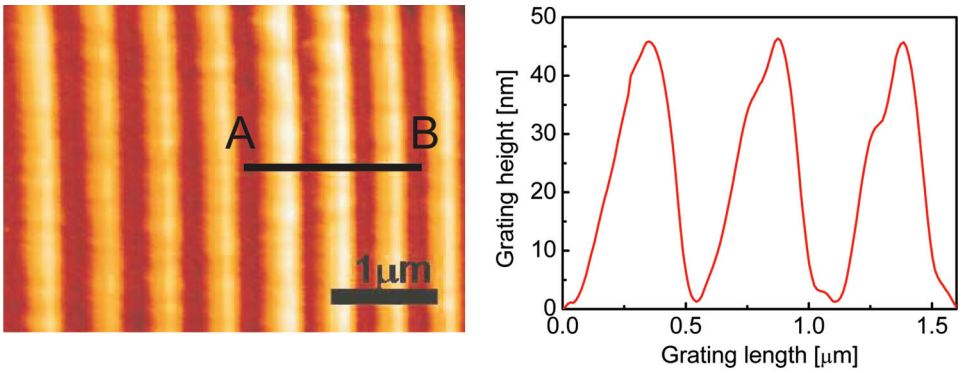

Figure 2. (a) AFM image of a grating structure with a period of 560 nm (b) Height profile of a grating structure with a period of 560 nm.

Figure 3 shows the structure of the LC cell used to observe the alignment abilities of the fabricated grating structures. The cover glass with the grating structure was used as one side of the cell. As a counter substrate, a glass substrate coated with rubbed polyimide (JSR: AL 1254) was used. When making a sandwich cell, the rubbing direction was set to 88 degrees to the groove direction of the structure. The cell was then filled with 5CB and observed under a polarization optical microscope (POM) (Nikon: Eclipse E600 POL) at approximately 21°C.

Results and Discussion

Figure 4 shows the POM images of a 14.9 μm-thick LC cell with a grating structure with period of 420 nm. The square region in the center of the image has the grating structure. Under a pair of crossed polarizers, the region with the grating structure appeared in a bright state. This suggests that liquid crystal underwent twisted nematic alignment in the region. Namely LC molecules on the fabricated grating were aligned along the grooves of micro-grating structures.

Next, we measured the azimuthal anchoring energy of the grating structure with a sinusoidal-like shape using the torque balance method [4,5] and compared them with a theoretical value of the grating-induced anchoring energy obtained according

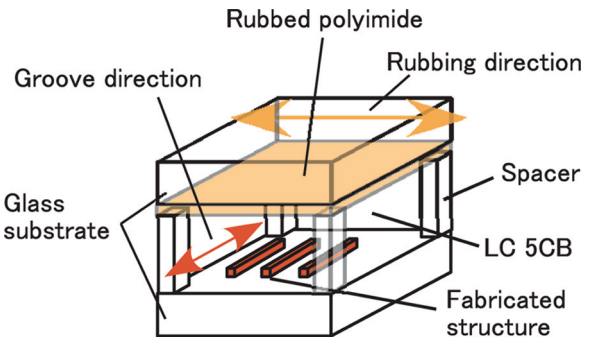

Figure 3. Cell structure of a LC cell.

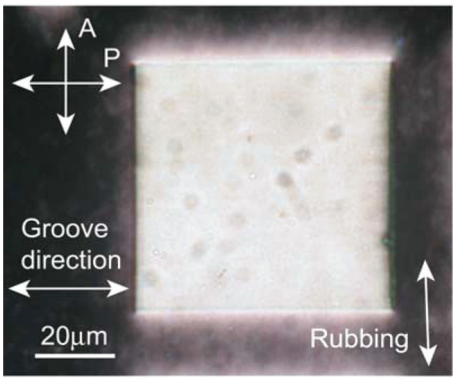

Figure 4. POM images of the fabricated grating in a LC cell. P, A are the directions of the polarizer and analyzer, respectively.

to Berreman's model [6,7]. An 11 μm-thick LC cell with the rubbing direction of PI aligned perpendicular to the groove direction of the fabricated grating in Figure 2 was used. In current studies of the azimuthal anchoring energy using the torque balance method, it is usually assumed that the anchoring strength on one substrate is infinite or that two substrates of TN cells have same anchoring strengths.

Assuming infinite anchoring at the rubbed PI surface along the rubbing direction, the azimuthal anchoring is determined by the balance between the torque due to the bulk elasticity and that due to the surface anchoring, and is given by the following equation [4,5],

$$A_\phi = \frac{2K_{22}\Delta\phi}{d\sin[2(\Phi - \Delta\phi)]}. \tag{1}$$

here, K_{22}, d, $\Delta\phi$, Φ denote the twist elastic constant ($K_{22} = 4.4 \times 10^{-12}$ N) [8], the cell thickness, the actual twist angle between molecules on top and bottom substrates, the angle between the rubbing direction and groove direction, respectively. The measured twist angle value using the cell rotation method was $\Delta\phi = 85.2^\circ$, giving an anchoring energy of 7.1×10^{-6} J/m^2.

On the other hand, when the two substrates of a TN cell are prepared under the same condition, the azimuthal anchoring energy is given by the following equation [9],

$$A_\phi = \frac{2K_{22}\Delta\phi}{d\sin(\Phi - \Delta\phi)}. \tag{2}$$

here, K_{22}, d, $\Delta\phi$, Φ denote the twist elastic constant, the cell thickness, the actual twist angle, the angle between the rubbing direction of top and bottom substrates, respectively.

According to Berreman [6,7], the azimuthal anchoring energy at the surface of a sinusoidal grating is expressed as follows:

$$A_\phi = \frac{2\pi^3 A^2 K}{\Lambda^3}. \tag{3}$$

where A is the height, Λ is the period of the grating, and K is the mean of the splay and bend elastic constants ($K = (K_{11} \times K_{33})^{1/2}$) ($K_{11} = 7.0 \times 10^{-12}$ N,

$K_{33} = 9.7 \times 10^{-12}$ N) [8]. Using a grating period of $\Lambda = 519$ nm and grating height of $A = 46$ nm, an anchoring energy of 7.7×10^{-6} J/m^2 was calculated by this method. A good agreement is observed between experimentally and theoretically obtained anchoring energies, suggesting that Berreman's theory is valid in this case for a shallow and sinusoidal-like shape of the grating. The slight disparity between two results may have contributed from experimental errors and minor deviation of the grating structure's shape from the ideal sinusoidal shape assumed in the Berreman model.

Next, we examined azimuthal anchoring energies of grating structures with various dimensions. We fabricated grating structures with heights of 270–1100 nm and periods of 3.5–14 μm which were confirmed under an AFM (KEYENCE: VN-8000). Grating heights can be controlled by laser intensity and we fabricated grating heights of 270–1100 nm with laser intensity of 4–16 MW/cm^2. The cover glass with the grating structure was used as one side of the cell. As a counter substrate, a glass substrate coated with rubbed PI was used. When making a sandwich cell, the rubbing direction was set to 88 degrees to the groove direction of the structure. The 14.9 μm-thick LC cell was then filled with 5CB.

The dependence of the azimuthal anchoring energy on grating heights is shown in Figure 5(a). This indicates that the azimuthal anchoring energy increases with increasing grating heights for any grating period. The grating-period dependence of the azimuthal anchoring energy is shown in Figure 5(b), which indicates that the azimuthal anchoring energy increases with decreasing grating periods for any grating height. In these cases, the shapes of grating structures didn't resemble a sinusoidal profile. To compare experimentally and theoretically obtained anchoring energies, it is necessary to think another theoretical model instead of the Berreman model.

We also compared the anchoring strength of the grating with that of a rubbed PI substrate. Two pieces of glass substrates coated with rubbed PI were used as cell substrates. When making a sandwich cell, the rubbing direction on one substrate was set 90 degrees to the rubbing direction of the counter substrate. A cell with thickness of approximately 14.0 μm was used. The cell was then filled with 5CB and the azimuthal anchoring energy was obtained from Eq. (2).

The obtained energy for the rubbed substrate was 4.6×10^{-5} J/m^2 and was about one order larger than that for the grating surface, but using a thinner cell

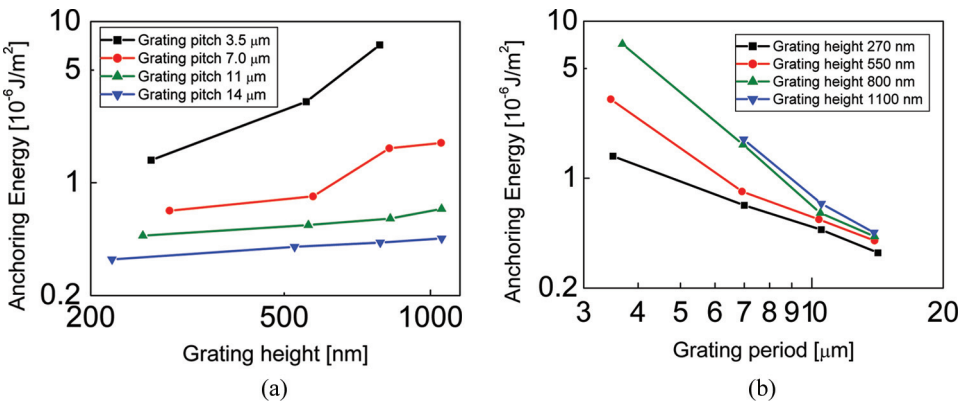

Figure 5. (a) The azimuthal anchoring energy dependence of grating height (b) The azimuthal anchoring energy dependence of grating period.

and other methods will allow the measurement of stronger anchoring strengths. Shortening grating periods or heightening grating heights will enable to allow the stronger anchoring strengths of the grating structure.

Conclusion

We have shown that one-dimensional micro-scale grating structures fabricated by TPE-DLW enable local control of the alignment of nematic LCs. We also found that the azimuthal anchoring energy of the grating is about one order weaker compared to substrates treated by the rubbing method, but varying heights and periods of the grating allows a relatively large control of the anchoring energy.

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