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Local liquid crystal alignment on patterned micrograting structures photofabricated by two photon excitation direct laser writing

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The authors demonstrate local alignment of nematic liquid crystal through the fabrication of local micrograting structures by curing an ultraviolet curable material via a two-photon excitation laser-lithography process. A local twisted-nematic region was prepared using one rubbed and one fabricated micrograting surface and the resulting cell was observed with a polarizing optical microscope. The polarization optical micrographs of the locally fabricated region suggest that liquid crystal molecules align parallel to the grating structure and that local alignment is achieved. We evaluate the anchoring energies of the fabricated microgratings by the torque balance method.

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Liquid crystal (LC) alignment plays a crucial role in displays and other LC devices. Large surface area alignment is usually achieved through the traditional method of rubbing and has been long used in the LC display industry. However, there is an ongoing search for noncontact or other methods of alignment in order to achieve a strong, uniform alignment without unwanted effects caused by static charges or dust easily introduced by the rubbing process. Furthermore, local alignment methods have attracted vast interests in recent years due to the various possibilities that they may allow: since the characteristics of LC devices depend significantly on the alignment of the LC molecules, controlling the LC alignment locally may allow findings of unprecedented LC properties and phenomena that may lead to intelligent optoelectronic devices. One of the local alignment methods that has been demonstrated recently used an atomic force microscope (AFM) to fabricate micropatterned local polyimide (PI) domains through the process of nanorubbing. 1,2 In their report, local LC alignment, bistability, and tristability of nematic LC (NLC) were achieved through the microdomains.

In this study, we propose a local alignment method where a laser-lithography method known as two-photon excitation direct laser writing³⁻⁵ (TPE-DLW) is used to fabricate microscale grating structures to locally control the LC alignment. Controlled with a computerized system, DLW not only allows fast and clean structure fabrication but also ease of designing various structure patterns. Moreover, compared to normal DLW, the usage of TPE process allows the extra advantage of fabricating even smaller structures, which would allow local LC orientation control at an even higher resolution. The resultant LC orientation characteristics and anchoring energies exhibited by the grating structures are reported here.

The light-curing material used in the micrograting 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 the absorption at $\lambda = 400$ nm and 0.1 wt % of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (Exciton: DCM) dye

The experimental setup for the fabrication process is schematically illustrated in Fig. 1(a). Experiments were performed under dark conditions to avoid unnecessary curing of the material. TPE-DLW was performed on a confocal laser scanning microscope (CLSM) system (Carl Zeiss: LSM 510). The target cover glass with the spin-coated material was positioned onto 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 was focused by a high numerical aperture oil-immersion objective lens $(63 \times, NA=1.4)$ and controlled by a galvanometer to scan arbitrarily within a maximum scanning area of $146.2 \times 146.2 \ \mu \text{m}^2$. Upon irradiation by the focused laser, the material lying in the vicinity of the focal point cures under the process of TPE due to the high photon density in that region. Laser lithography was performed at a laser intensity range of 1.7–6 MW/cm² and a scan speed of $8.96-179 \mu s/\mu m$. The material within the designated region was cured with a single scan under these laser conditions. The uncured material was removed by rinsing in acetone for

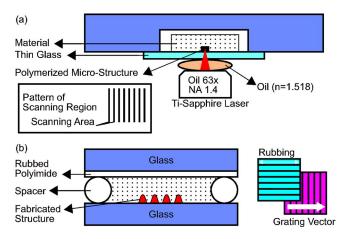


FIG. 1. (Color online) Schematic of (a) the experimental setup with the pattern of the scanning region and (b) structure of the LC cell.

for observation purposes. NOA 61 was chosen due to its fast curing time, good adhesion, and chemical stability. The NLC material used to demonstrate the alignment properties was 4-*n*-pentyl-4'-cyanobiphenyl (Merck: 5CB) ($n_o = 1.522$, $n_e = 1.706$).

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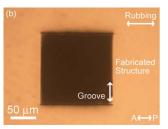


FIG. 2. (Color online) POM images of the fabricated grating in a LC cell. P and A are the directions of the polarizer and analyzer, respectively. (a) Crossed polarizers and (b) parallel polarizers.

10 s and ethanol for 30 s, so that the cover glass surface was left only with the cured micrograting structure.

Figure 1(b) 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. A piece of glass substrate coated with rubbed PI (JSR: AL 1254) was used as the countersubstrate. When fabricating the cell, the rubbing direction of the PI was aligned parallel to the grating vector of the structure; i.e., perpendicular to the groove direction of the fabricated grating. The cell was then filled with 5CB and observed under a polarization optical microscope (POM) (Nikon: Eclipse E600 POL) at approximately 21 °C.

Figure 2 shows the POM images of a $4-\mu$ m-thick LC cell with a grating structure with a period of 500 nm and a height of 600 nm. The square region in the center of the image is where the grating structures were fabricated. Under a pair of crossed polarizers [Fig. 2(a)], the region with the grating structure appeared bright. On the other hand, under a pair of parallel polarizers [Fig. 2(b)], the bright and dark regions were inverted and light extinction could be observed in the region with the grating structure. These observations indicated that the LC molecules on the fabricated grating structure were aligned along the grooves of the grating structure, forming a local twisted-nematic LC alignment within the LC cell.

The azimuthal anchoring energy of the grating structure was measured by the torque balance method^{6,7} and compared with the theoretical value obtained by Berreman's model.^{8,9} The profile of the grating was measured by an AFM (JEOL: JSPM-4210) (Fig. 3) and a cell with thickness approximately $11 \mu m$ was used.

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 and that due to surface anchoring and is expressed by the following equation: ^{6,7}

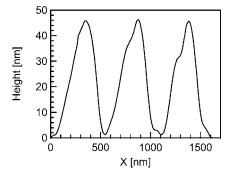


FIG. 3. Height profile of a grating structure with a period of 519 nm.

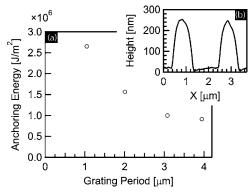


FIG. 4. (a) Relationship between the grating period and surface azimuthal anchoring energy measured by the torque balance method. (b) Height profile of a grating structure with a period of 2 μ m.

$$A_{\phi} = \frac{2K_{22}\phi_T}{d\sin 2\Delta\phi},\tag{1}$$

where $\phi_T = \phi_T^0 - \Delta \phi$. Here, K_{22} , d, ϕ_T , ϕ_T^0 , and $\Delta \phi$ denote the twist elastic constant $(K_{22} = 2/3 \times K_{11}; K_{11} = 7.12 \times 10^{-12} \text{ N})$, the cell thickness, actual twist angle, the angle between the rubbing direction and groove direction of the grating, and the deviation angle, respectively. The measured twist angle value was $\phi_T = 85.2^\circ$, giving an anchoring energy of $7.7 \times 10^{-6} \text{ J/m}^2$.

According to Berreman, ^{8,9} the azimuthal anchoring energy at the surface of a sinusoidal grating is expressed as follows:

$$W_B = \frac{2\pi^3 A^2 K}{\Lambda^3},\tag{2}$$

where A is the height, Λ is the period of the grating, and K is the mean of the splay and bend elastic constants $[K=(K_{11} \times K_{33})^{1/2}]$ ($K_{33}=9.82\times 10^{-12}$ N). Using a grating period of $\Lambda=519$ nm and grating height of A=46 nm obtained from the AFM measurements, an anchoring energy of 7.9 $\times 10^{-6}$ J/m² was obtained. A good agreement is obtained between the experimentally and theoretically obtained anchoring energies, indicating that Berreman's theoretical model is applicable to structures fabricated by TPE-DLW when the grating is relatively shallow and the shape resembles a sinusoidal profile. The slight disparity between the two results may have resulted from experimental errors or minor deviation of the grating structure's shape from the ideal sinusoidal shape assumed in the Berreman model.

Finally, to observe the relationship between the azimuthal anchoring energy and the grating period, the azimuthal anchoring energies for gratings with a height of approximately 250 nm and periods of $1-4~\mu m$ were measured using the torque balance method [Fig. 4(a)]. The anchoring energy was observed to be in the order of $10^{-6}~J/m^2$. The grating profile shown in Fig. 4(b) indicates that the shape of the grating deviates greatly from a sinusoidal profile (such as that shown in Fig. 3) as the grating period increases. Although the Berreman model is not applicable here due to this deviation, Fig. 4(a) indicates that the azimuthal anchoring energy is inversely proportional to the grating period, which agrees to a certain extent with the inversely proportional relationship between the grating period and anchoring energy presented in Berreman's theory.

In conclusion, we fabricated local micropatterned grating structures from a UV-curable polymer by means of TPE-DLW and demonstrated local alignment of NLCs above the structures. Fabrication time is short since only one scan of the laser at a scan speed of less than 179 μ s/ μ m is needed to fabricate the uniform grating structures. We have shown that for a shallow structure with a period of 519 nm and a height of 46 nm, the anchoring energy can be modeled by using the Berreman model for a sinusoidal grating. We also found the azimuthal anchoring energy to be inversely proportional to the grating period by using the torque balance method.

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