INVITED PAPER *Special Section on Electronic Displays*

Fabrication of Micro-Grating Structures by Direct Laser Writing Based on Two Photon Process and Their Liquid Crystal Alignment Abilities

Chee Heng LEE[†], ***Nonmember***, **Hiroyuki YOSHIDA**[†], ***Member***, **Yusuke MIURA**[†], ***Nonmember***, **Akihiko FUJII**[†], ***Member***, ***and*** **Masanori OZAKI**[†a)], ***Nonmember***

SUMMARY The authors have demonstrated the local alignment of nematic liquid crystal with local micro-grating structure fabricated by the curing of an ultraviolet curable material via a three dimensional micro-fabrication technique known as two photon excitation direct laser writing [1]. The molecular alignment of the nematic liquid crystals on the fabricated micro-grating structures was firstly investigated by the observations of a local twisted nematic region in a liquid crystal cell made of a substrate with locally fabricated micro-grating structure and a counter substrate with rubbed polyimide. The optical polarizing microscope observation of the micro-grating structures indicated that liquid crystals molecules have aligned parallel to the grooves of the micro-grating structure and that local alignment was successfully achieved. The alignment characteristics of the liquid crystals on these micro-gratings was also investigated and discussed quantitatively in details through the measurement of anchoring energy by the conventional torque balance method and the Berreman method. The azimuthal anchoring energy for the micro-grating was found to be in the order of 10^{-6} J/m^2 and inversely proportional to the grating period.

key words: *photo-fabrication, liquid crystal alignment, two photon excitation, grating*

1. Introduction

The importance of a precise and reliable control of liquid crystal (LC) alignment on the surfaces of liquid crystal displays (LCDs) has accelerated development of new alignment techniques, from the more traditional rubbing method initially proposed by Mauguin [2], which involves the rubbing of a surface with a polymer cloth, to recent clean non-rubbing techniques such as photo-alignment [3]. In recent years, however, with the rapid development of nanotechnology, the possibilities and advantages of controlling LC molecules on a local level rather than the conventional large area alignment techniques as mentioned earlier, started to attract vast interests. Since the characteristics of LC devices depend predominantly on the alignment of the LC molecules, controlling the LC alignment locally with high precision and reliability, may allow findings of new LC properties, phenomenon and hence allowing the exploration of new LC devices in the future. Because of these exciting prospects, developments on local LC alignment have started to gather pace recently. One of the local alignment methods that has been successfully demonstrated recently, used an atomic force microscope (AFM) to fabricate micro-patterned local polyimide (PI) domains through the process of nano-rubbing [4], [5]. In their report, local LC alignment, bistability and tristability of nematic LC (NLC) was successfully achieved on the fabricated local micro-domains.

The LC groove alignment phenomenon was firstly reported by Berreman [6] and so far, has repetitively successfully demonstrated by the alignment of LC on periodic gratings on alignment layers produced by reactive-ion etching [7], [8], photolithography [9], [10] and stamped morphology [11]. In this study, we propose a new local alignment method where the alignment of LC is controlled locally through micro-scale grating structures fabricated from a light-curing material using a laser lithography method known as two-photon excitation direct laser writing (TPE-DLW) [12]–[15]. TPE-DLW is a three dimensional micro-fabrication technique which was originally proposed by S. Maruo et al. [12] and commonly used nowadays in the fabrication of photonic crystals [16]. Compared to the normal DLW, the usage of TPE process together with DLW allows the extra advantage of fabricating finer structures since TPE only takes place in the vicinity of the focus point. Although only micro-gratings was fabricated in this study, with the usage of the computerized confocal laser scanning microscope (CLSM) system, local structures with arbitrary shapes could be designed and fabricated easily three dimensionally and thus, bringing the possibility of investigation of local LC alignment by complicated three-dimensioned structures in future investigations.

Since anchoring plays an important role in determining the bulk alignment of liquid crystalline phases, and thereby the electro-optical properties of LC-based devices, the alignment characteristics displayed by the LCs over these micro-gratings will also be investigated and discussed quantitatively in details in this paper through the measurement of anchoring energies.

2. Material

In this study, the material used for undergoing the photo-polymerization via the TPE-DLW in the micro-grating fabrication process was prepared by mixing a colorless urethane-based ultraviolet (UV)-curable photopolymer, Norland Op-

Manuscript received March 3, 2008.
Manuscript revised May 13, 2008.
[†]The authors are with the Graduate School of Engineering, Osaka University, Suita-shi, 565-0871 Japan.
a) E-mail: ozaki@eei.eng.osaka-u.ac.jp
DOI: 10.1093/ietele/e91–c.10.1581

tical Adhesive 61 (NOA 61), with 0.1 wt% of Irgacure 819 (phosphine oxide, phenyl bis(2,4,6-trimethylbenzoy)) (Ciba) and 0.1 wt% of DCM dye (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran) (Exciton). NOA 61 was chosen due to its fast curing time, good adhesion and solvent resistance once fully cured. Irgacure 819 was doped into the mixture so as to enhance the polymerization rate for light at the wavelength of 400 nm, a wavelength which was used here in this study for TPE process. On the other hand, DCM was doped into the mixture for observation purposes during the micro-fabrication process.

The LC material used for demonstrating the alignment properties induced was the NLC 4-n-pentyl-4′-cyanobiphenyl (5CB) (Merck) ($n_o = 1.522$, $n_e = 1.706$) at room temperature. The elastic constants of 5CB used for the calculation of anchoring energies are $K_{11} = 7.12 \times 10^{-12}$ N; $K_{22} = 2/3 \times K_{11}$; $K_{33} = 9.82 \times 10^{-12}$ N [17].

3. Experimental

The experimental stage setup in this study used to carry out TPE-DLW is schematically illustrated in Fig. 1.

Experiments were performed under dark conditions to avoid unnecessary curing of the material. TPE-DLW was performed using a CLSM system (Carl Zeiss: LSM 510). 100 fs pulses of a titanium sapphire laser with a repetition rate of 82 MHz (Spectra Physics: Maitai) are focused on a target cover glass ($18 \times 18\,\text{mm}^2$) which was spin-coated with a light-curing material and mounted onto the stage of the CLSM system as shown in Fig. 1. The laser was focused via a high numerical aperture oil-immersion objective lens (63x, N.A = 1.4, W.D = 0.19 mm) and controlled by an internal computerized galvanometer of the CLSM to scan arbitrarily within a maximum square scanning area of $146.2 \times 146.2\,\mu\text{m}^2$. Upon irradiation with the focused laser, photopolymerizaion is induced in the material lying in the vicinity of the point of focus under the process of TPE due to the high density of photons concentrating in that region.

Laser lithography was performed at a laser intensity range of $1.7 \sim 6\,\text{MW/cm}^2$ and scan speed of $1.4 \sim 112$ mm/s. Under these laser conditions, only a single laser scan across the designated area was required for the photopolymerization of the material in that region. With the help of the computerized system of the CLSM, arbitrary regions in a certain focused region could be selected easily to be subjected to photo-polymerization. In this study, a square region containing selected line regions as shown in Fig. 1 was used in order to fabricate local micro-grating structures. After the polymerized region was fabricated within the material by TPE-DLW, the remaining unpolymerized material surrounding the polymerized region was rinsed away with firstly acetone for 10 s, followed by ethanol for 30 s, leaving only the cured polymer micro-grating structure on the surface of the cover glass. Excess rinsing was avoided to prevent unnecessary damage to the resultant polymerized region left on the cover glass substrate.

After the micro-grating structures were successfully

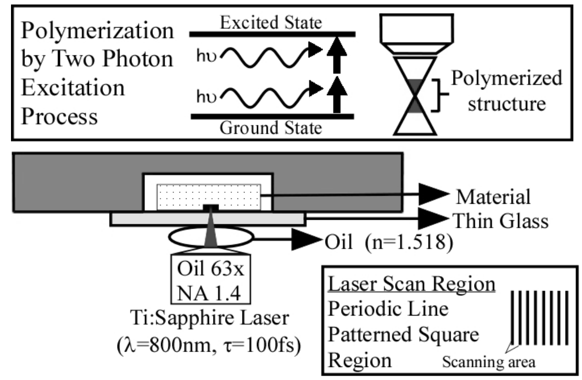

Fig. 1 Schematic diagram of the experimental stage setup with the pattern of the scanning region.

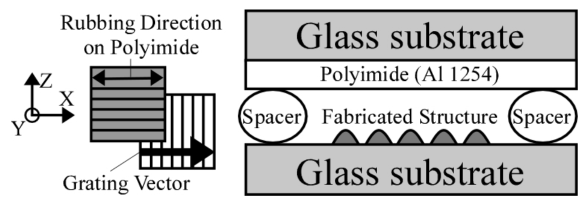

Fig. 2 Cell structure of a LC cell.

fabricated, a LC cell setup as shown in Fig. 2 was used to observe the alignment abilities of the locally fabricated micro-grating structures. For this setup, the cover glass with the fabricated grating structure was used for one side of the cell. As for the counter substrate, a piece of glass substrate coated with rubbed polyimide (PI) (JSR: AL 1254) was used. Here, the rubbing direction of the PI was aligned parallel to the grating vector of the structure, or in other words, perpendicular to the groove direction of the fabricated grating. The cell was then filled with 5CB and observed under an optical polarizing microscope (Nikon: Eclipse E600 POL) at room temperature.

4. Results and Discussion

In Fig. 3, it was observed that a micro-grating structure was successfully fabricated by the TPE-DLW.

For this particular structure, it was fabricated with a laser intensity of $3.41\,\text{MW/cm}^2$, a laser scan speed of 5.6 mm/s and has a period of around 500 nm, a height of around 600 nm, and a surface area of $146.2 \times 146.2\,\mu\text{m}^2$. Micro-grating with regular gratings was observed to be successfully fabricated with the laser conditions mentioned above.

The dependence of the structure's height on both the intensity and the scan speed of the laser beam were investigated and shown in Fig. 4. The laser scan speeds used for fabricating the 2 sets of structures were 1.4 mm/s and 112 mm/s. From Fig. 4, it could be observed that the structure height increased proportionally with increasing laser intensity, regardless of the laser scan speed. In addition, from Fig. 4, the height of the structures was also observed to be

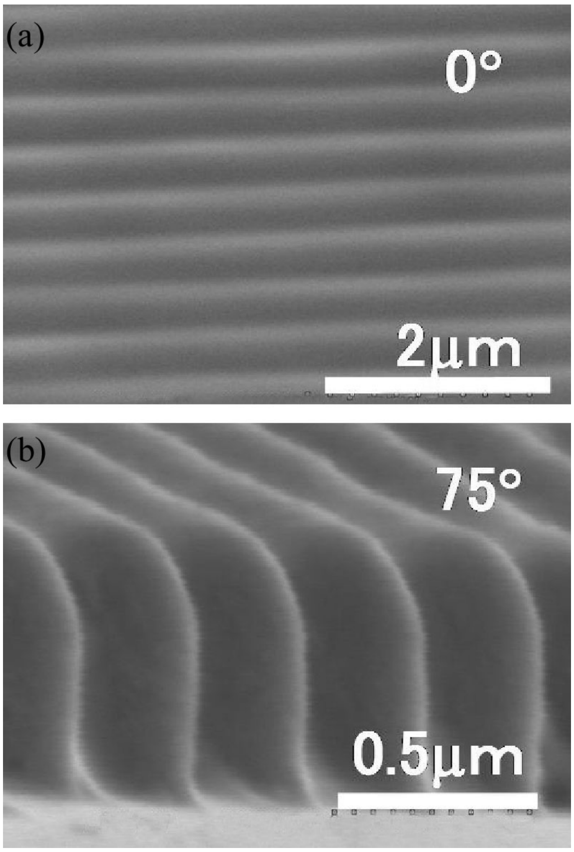

Fig. 3 SEM images of a micro-grating fabricated by TPE-DLW. (a) Overhead view (b) Side view taken at an angle of 75°.

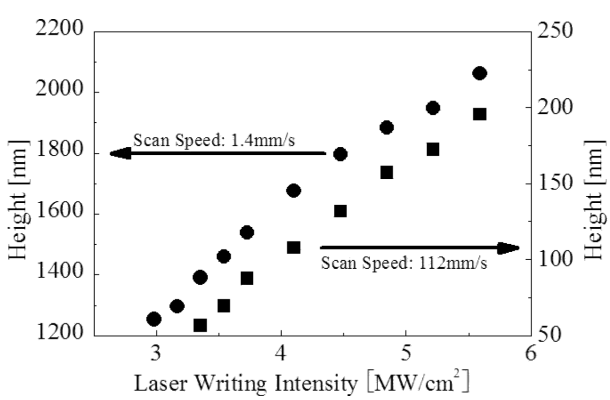

Fig. 4 Dependence of structure's height on intensity and scan speed of the laser beam.

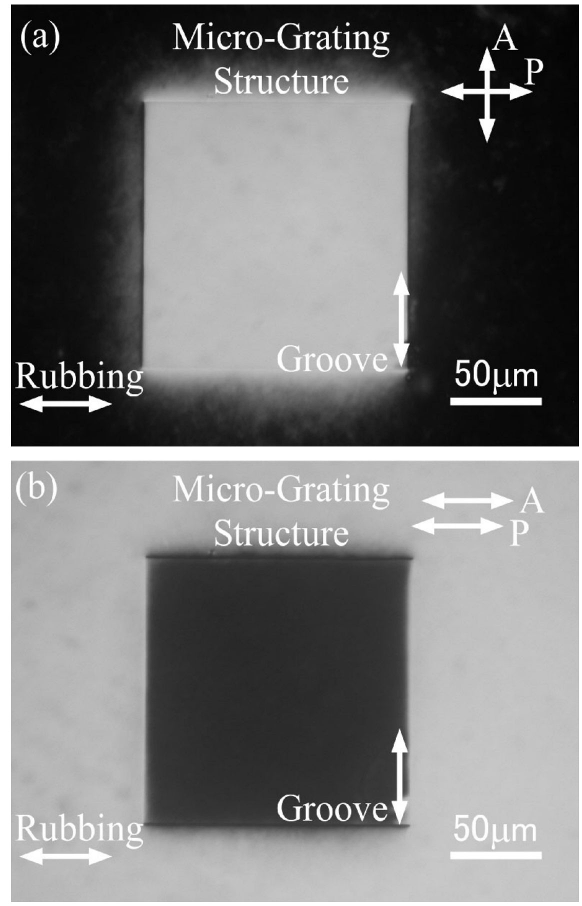

Fig. 5 Optical polarizing micro-photographs of fabricated grating enclosed in a LC cell. P, A represent the direction of the polarizer, analyzer respectively. (a) Crossed polarizers (b) Parallel polarizers.

dependent on the scan speed of the laser beam, decreasing from a range of approximately 1200 nm ~ 2000 nm (scan speed of 1.4 mm/s) to a range of approximately 50 ~ 200 nm (scan speed of 112 mm/s) when structures were fabricated with laser intensities of approximately 3 ~ 6 MW/cm^2 at the respective scan speed.

Next, the LC alignment abilities of the micro-grating structure in Fig. 3 was investigated by observing a 4 μm-thick LC cell, with the same cell setup as in Fig. 2 with an optical polarizing microscope. Figure 5 shows the optical polarizing micro-photographs of the LC cell with the square region containing the fabricated local grating structures in the center of the each image. Under a pair of crossed polarizers (Fig. 5(a)), the region with the grating structure appeared in the bright state. This suggests that the LC molecules on top of the structure probably underwent a near 90° rotation, and this in turn affected the incident light polarization, making it underwent by the same amount of rotation, and thus allowing it to pass through the analyzer, resulting in the bright state. Outside the square area with grating structure, there is a unidirectionally rubbed polyimide layer on a counter glass surface of the sandwich cell. As the result, uniform planar alignment could be realized and the complete extinction is obtained. Observation under a pair of parallel polarizers (Fig. 5(b)), on the other hand, showed that these bright and dark state regions were oppositely reversed and that light extinction could be observed in the region with the micro-grating structure. These results indicate that LC molecules on the fabricated grating structure were aligned along the grooves of the grating structure, forming a local twisted nematic (TN) LC alignment within the LC cell.

The main advantage of TPE-DLW is the ability to fabricate structures with arbitrary shapes and this was suc-

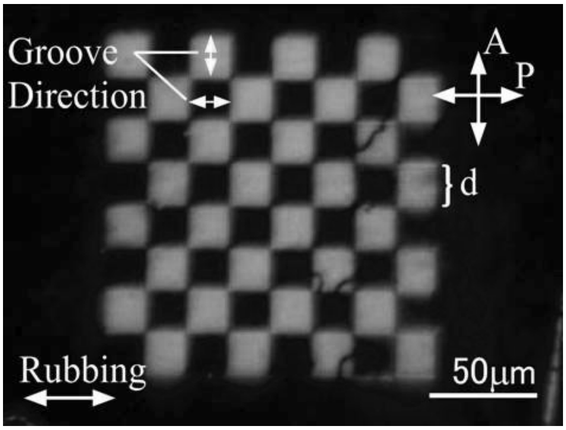

Fig. 6 Optical polarizing micro-photographs of a checkerboard structure (d = 19 μm) with domains of alternate groove directions at 90° to each other. P, A represent the direction of the polarizer, analyzer respectively.

cessfully demonstrated in Fig. 6. In this LC cell, a fabricated checkerboard structure containing 64 square domains (d = 19 μm) of alternate groove directions at 90° to each other was used. Under a pair of crossed polarizers, alternate homogenous and TN alignment regions were observed on the structure and this suggests that LC was successfully align along the alternate groove directions in the respective domains. Using TPE-DLW, domains with sides as small as 1 μm was successfully fabricated.

Next, the anchoring energy involved during such a local LC alignment by a groove structure fabricated by TPE-DLW was investigated by measuring the azimuthal anchoring energy experienced by NLC on a thin film micro-grating structure with a sinusoidal-resembled shape (Fig. 7) using both the conventional torque balance method [18], [19] and the Berreman's model [20]. An 11 μm-thick TN LC cell with a cell setup similar to that shown in Fig. 1(b) 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 elasticity and that due to surface anchoring, and is expressed by the following equation obtained from the elastic theory of the NLC and used in the torque balance method [18],

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

where $\Delta\phi = \phi_T^0 - \phi_T$. Here, K_{22}, d, ϕ_T, ϕ_T^0, $\Delta\phi$ denote the twist elastic constant, the cell thickness, actual twist angle, the angle between the rubbing direction and groove direction of the grating, and the deviation angle between ϕ_T^0 and ϕ_T, respectively. Using a measured twist angle value of 85.2°, the anchoring energy for this grating structure was calculated to be 7.7×10^{-6} J/m^2.

On the other hand, with Berreman's model, assuming sinusoidal-shaped gratings, the azimuthal anchoring energy at the grating surface can be expressed as follows:

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

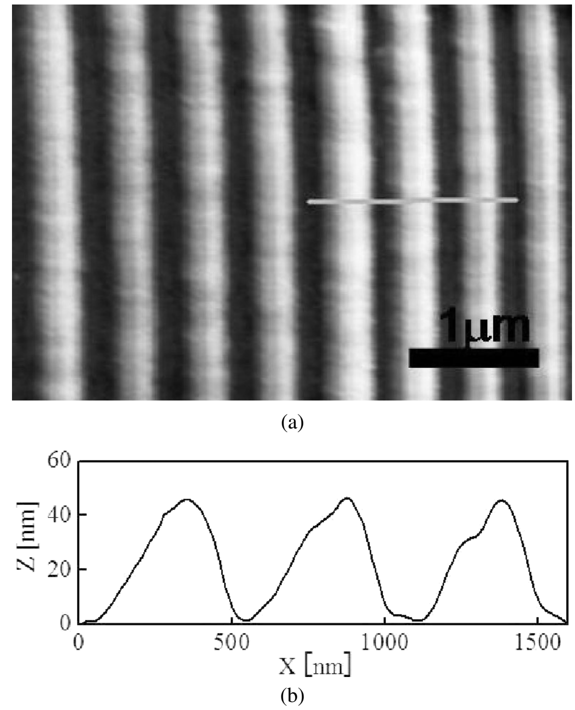

Fig. 7 AFM (a) image and (b) height profile of the fabricated grating used for the estimation of the anchoring energy. The line in the center of (a) is the line along which the height profile is taken. For this grating period, the shape of the grating structure is sinusoidal-resembled.

where A is the amplitude, λ is the pitch of the grating, and K is the mean of the splay and bend elastic constants ($K = (K_{11} \times K_{33})^{1/2}$). With a grating period of 519 nm and a grating height of 46 nm measured by the AFM (JEOL: JSPM-4210) (Fig. 7(b)), an anchoring energy of 7.9×10^{-6} J/m^2 was calculated by this method. Comparison between the two results obtained by Eqs. (1) and (2) suggests that a good agreement was observed between the results and that Berreman's theory is valid in this case for a shallow grating with the slight disparity between the two results contributed by both experimental errors and minor deviation of the grating structure's shape from the ideal sinusoidal shape assumed in the Berreman model. The applicability of the Berreman model on shallow grating from this result also agrees with the findings by Kimura et al. [17], where they have reported the applicability of Berreman model for shallow grating surfaces through the comparison of anchoring energies measured by the Berreman model and the finite element method.

Next, by fabricating micro-grating structures with arbitrary grating periods via TPE-DLW, the relationship between azimuthal anchoring energy and grating period was also investigated. The azimuthal anchoring energies for gratings with a common height of approximately 250 nm and different periods of 1∼4 μm were experimentally measured using the torque balance method and shown in Fig. 8(a). Here, a 10.5 μm-thick TN LC cell with a cell setup similar to that shown in Fig. 2 was used. From Figs. 8(b)–(e), it could be observed that as the grating period increases, the shape of the grating structure deviated from

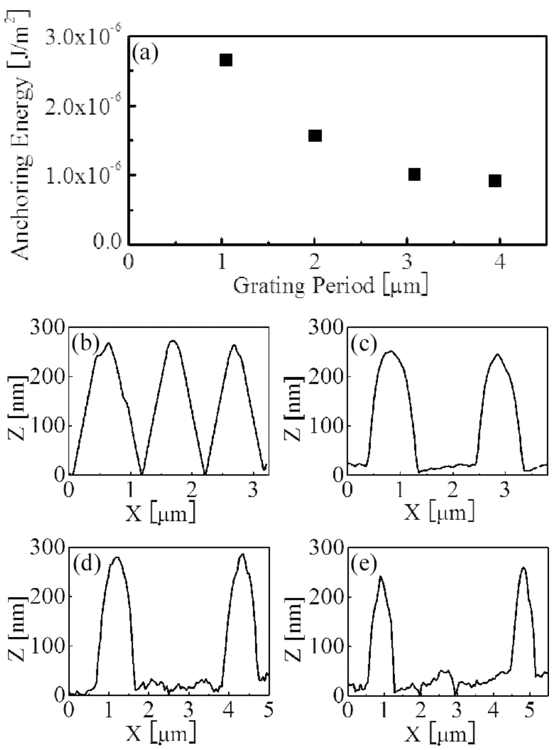

Fig. 8 Relationship between grating period and surface azimuthal anchoring energy measured by torque balance method. (b)~(e) Height profile of a grating structure with a period of $1\,\mu$m, $2\,\mu$m, $3\,\mu$m and $4\,\mu$m respectively.

the sinusoidal-resembled shape observed for a grating structure of approximately 500 nm (Fig. 7) and even more from the ideal sinusoidal shape assumed in the Berreman model. From Fig. 8(a), it could be observed that the anchoring energy was in the order of 10^{-6} J/m^2 and that the azimuthal anchoring energy was inversely proportional to the grating period. Although the Berreman model was not applicable here due to the deviation from a sinusoidal grating, the inverse proportional relationship between azimuthal anchoring energy and grating period observed in Fig. 8(a) agrees to a certain extent with the inverse proportionality relationship between grating period and anchoring energy related in the Berreman's theory.

5. Conclusions

In conclusion, we have proposed a new local LC alignment method where a laser lithography process known as TPE-DLW was used and demonstrated that local micro-patterned grating structures photo-fabricated from a UV-curable photopolymer via TPE-DLW can be used to locally align NLC. Fabrication time is short since only one scan of the laser at a scan speed of more than 1.4 mm/s is needed to fabricate the uniform grating structures. We have also shown that for a shallow structure with a period of 519 nm and a height of 46 nm, the anchoring energy obtained by the Berreman model is applicable since it agrees with the measured value by the torque balance method with small disparity. Lastly, the azimuthal anchoring energy was also found to be inversely proportional to the grating period by the torque balance method.

Acknowledgments

This work is partly supported by a Global COE program, "Center for Electronic Devices Innovation", and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] C.H. Lee, H. Yoshida, Y. Miura, K. Tokuoka, A. Fujii, and M. Ozaki, "Patterned LC alignment on micro-grating structures fabricated by direct laser writing," Proc. IDW'07, pp.409–412, 2007.
[2] C. Mauguin, "Sur les cristaux liquides de Lehmann," Bull. Soc. Fr. Min., vol.34, pp.71–117, 1911.
[3] W. Gibbons, P. Shannon, S. Shao-Tang, and B. Swetlin, "Surface-mediated alignment of nematic liquid crystals with polarized laser light," Nature, vol.351, pp.49–50, 1991.
[4] J.-H. Kim, M. Yoneya, and H. Yokoyama, "Tristable nematic liquid-crystal device using micropatterned surface alignment," Nature, vol.420, pp.159–162, 2002.
[5] J.-H. Kim, M. Yoneya, J. Yamamoto, and H. Yokoyama, "Surface alignment bistability of nematic liquid crystals by orientationally frustrated surface patterns," Appl. Phys. Lett., vol.78, no.20, pp.3055–3057, 2001.
[6] D.W. Berreman, "The alignment of liquid crystlas by grooved surfaces," Mol. Cryst. Liq. Cryst., vol.23, pp.215–231, 1973.
[7] D.C. Flanders, D.C. Shaver, and H.I. Smith, "Alignment of liquid crystals using submicrometer periodicity gratings," Appl. Phys. Lett., vol.32, no.10, pp.597–598, 1978.
[8] J. Cheng and G.D. Boyd, "The liquid-crystal alignment properties of photolithographic gratings," Appl. Phys. Lett., vol.35, no.6, pp.444–446, 1979.
[9] G.P. Bryan-Brown, J.R. Sambles, and K.R. Welford, "Grating coupled liquid crystal waveguides using nematics and smectics," J. Appl. Phys., vol.73, no.8, pp.3603–3607, 1993.
[10] Y. Kawata, K. Takatoh, M. Hasegawa, and M. Sakamoto, "The alignment of nematic liquid crystals on photolithographic micro-groove patterns," Liq. Cryst., vol.16, no.6, pp.1027–1036, 1994.
[11] E.S. Lee, P. Vetter, T. Miyashita, T. Uchida, M. Kano, M. Abe, and K. Sugawara, "Control of liquid crystal alignment using stamped-morphology method," Jpn. J. Appl. Phys., vol.32, no.10A, pp.L1436–L1438, 1993.
[12] S. Maruo, O. Nakamura, and S. Kawata, "Three-dimensional microfabrication with two-photon-absorbed photopolymerization," Opt. Lett., vol.22, pp.132–134, 1997.
[13] S. Kawata, H. Sun, T. Tanaka and K. Takada, "Finer features for functional microdevices," Nature, vol.412, pp.697–698, 2001.
[14] W. Haske, V.W. Chen, J.M. Hales, W. Dong, S. Barlow, S.R. Marder, and J.W. Perry, "65 nm feature sizes using visible wavelength 3-D multiphoton lithography," Opt. Express, vol.15, no.6, pp.3426–3436, 2007.
[15] H. Yoshida, C.H. Lee, A. Fujii, and M. Ozaki, "Tunable single photonic defect-mode in cholesteric liquid crystals with laser-induced local modifications of helix," Appl. Phys. Lett., vol.89, no.23, p.231913, 2006.
[16] M. Deubel, G. von Freymann, M. Wegener, S. Pereira, K. Busch, and C.M Soukoulis, "Direct laser writing of three-dimensional photonic-crystal templates for telecommunications," Nat. Mater., vol.3, pp.444–447, 2004.
[17] M. Kimura, Y. Ohta, and T. Akahane, "Surface azimuthal anchoring energy between the trapezoid grating surface and nematic liquid

crystal layer studied by finite element method," Adv. in Tech. of Mater. and Mater. Proccessing, vol.7, pp.91–96, 2005.
[18] Y. Ohta, N. Tanaka, M. Kimura, and T. Akahane, "Surface azimuthal anchoring energy between the grating surface and nematic liquid crystal layer studied by finite element method," Jpn. J. Appl. Phys., vol.43, no.7A, pp.4310–4311, 2004.
[19] T. Akahane, H. Kaneko, and M. Kimura, "Novel method of measuring surface torsional anchoring strength of nematic liquid crystals," Jpn. J. Appl. Phys., vol.35, no.8, pp.4434–4437, 1996.
[20] D.W. Berreman, "Solid surface shape and the alignment of an adjacent nematic liquid crystal," Phys. Rev. Lett., vol.28, no.26, pp.1683–1686, 1972.

Chee Heng Lee was born in Singapore in 1980. He received his B.E. degree in Electronic Engineering from Osaka University (Japan) in 2006. He will be finishing his M.S. degree in 2008. His main research interests include liquid crystal alignment and photo-fabrication.

Hiroyuki Yoshida received his M.S. degree (2006) in Electronic Engineering from Osaka University in Japan, and is currently finishing his Ph.D. degree. He has received presentation awards from the Japanese Society of Applied Physics and the Kansai-section Joint Convention of Institutes of Electrical Engineering (2005), and at the International Conference on Nano-Molecular Electronics (2006).

Yusuke Miura was born in 1983. He received his B.E. degree in Electronic Engineering from Osaka University (Japan) in 2007. He is currently engaged in the research related to liquid crystal alignment characteristics as a 1st-year master's degree student at Osaka University.

Akihiko Fujii was born in Osaka, Japan in 1969. He received his B.E., M.E., and D.E. degrees from Osaka University in 1993, 1995, and 1997, respectively. After one-year JSPS fellowship, he joined Department of Electronic Engineering in Osaka University as a research associate in 1998, and was promoted to an Associate Professor in Division of Electrical, Electronic and Information Engineering, Graduate School of Engineering, Osaka University in 2006. He has been engaged in research on optical and electrical devices utilizing organic materials including dye molecules and conducting polymers. He is a member of the Japan Society of Applied Physics, and the Society of Polymer Science, Japan.

Masanori Ozaki received his B.E., M.E., and D.E. degrees from Osaka University in 1983, 1995, and 1988, respectively. He joined Department of Electronic Engineering in Osaka University as a research associate in 1988, and was promoted to an Associate Professor in 1994 and to a Professor in 2005. He has been engaged in the research on physical properties and applications of organic functional materials, particularly liquid crystals and conjugated polymers. He stayed in Physics Department at the University of Utah from 1994 to 1995 as a visiting scientist and studied spectroscopy of conjugated polymers. He obtained Best Paper Award of Japan Liquid Crystal Society. His current research interests are nano-structured organic materials and their application to electronic and photonic devices.