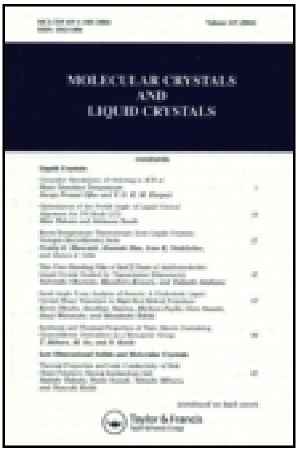
This article was downloaded by: [Moskow State Univ Bibliote]
On: 15 April 2012, At: 12:20
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Controlling Orientation Direction of Discotic Columns Assembled in Microtrenches

Cheng-Yan Chiang [a], Ian Underwood [b] & Wenjun Zheng [a]

[a] Department of Photonics, National Sun Yat-Sen University, 70 Lien-Hai Road, Kaohsiung 804, Taiwan, R.O.C.

[b] School of Engineering, The University of Edinburgh, The King's Buildings, Mayfield Road, Edinburgh, EH9 3JF, UK

Available online: 11 Jan 2012

To cite this article: Cheng-Yan Chiang, Ian Underwood & Wenjun Zheng (2012): Controlling Orientation Direction of Discotic Columns Assembled in Microtrenches, Molecular Crystals and Liquid Crystals, 553:1, 185-192

To link to this article: http://dx.doi.org/10.1080/15421406.2011.609469

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., Vol. 553: pp. 185–192, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.609469

Taylor & Francis
Taylor & Francis Group

Controlling Orientation Direction of Discotic Columns Assembled in Microtrenches

CHENG-YAN CHIANG,[1] IAN UNDERWOOD,[2] AND WENJUN ZHENG[1,*]

[1]Department of Photonics, National Sun Yat-Sen University, 70 Lien-Hai Road, Kaohsiung 804, Taiwan, R.O.C.
[2]School of Engineering, The University of Edinburgh, The King's Buildings, Mayfield Road, Edinburgh EH9 3JF, UK

Downloaded by [Moskow State Univ Bibliote] at 12:20 15 April 2012

Microtrenches have been produced on the surface of a glass substrate using conventional photolithography technique. When subsequently deposited on the micro-patterned substrate, discotic triphenylene molecules are found to assemble into columns with orientational ordering. Homogeneous alignment of the discotic columns has been produced on the substrate with parallel microtrenches. The orientational direction of the discotic columns can be controlled using a set of controlling microtrenches. By properly modifying the topological structures of the controlling microtrenches we are able to tune the discotic columns assembled in the primary trenches to align either parellel or perpendicular to the walls of the trenches.

Keywords disc-like molecules; microtopological patterned surface; microtrench; discotic column orientation; discotic column alignment

1. Introduction

Discotic compounds, which consist of disk-like molecules, have attracted more and more attention due to their versatility in many applications. When the molecules assemble into a highly ordered columnar structure, discotic compounds have been shown to exhibit unique orientation-dependent effects such as one-dimensional charge-carrier mobility [1–3] and polarized emission [4, 5]. Therefore, discotic compounds are thought to have the potential for use in organic devices that require an efficient unidirectional charge transport. Indeed, they have already been found to have uses in photovoltaic cells [6, 7], light-emitting diodes [8, 9], and organic semiconductor transistors [10, 11]. These applications require a highly oriented columnar structure with long-range ordering in a specific way. For example, homogeneous alignment of discotic compound, with discotic columns lying parallel to the substrate, is required for field-effect transistors. On the other hand, homeotropic alignment of the discotic compound, with the columns orienting perpendicular to the substrate (and the electrodes), is desired in photovoltaic cells and light-emitting diodes. Over the years, many attempts have been made to obtain an ordered assembly of the discotic molecules in

*Address correspondence to Wenjun Zheng, Department of Photonics, National Sun Yat-Sen University, 70 Lien-Hai Road, Kaohsiung 804, Taiwan, R.O.C. E-mail: wzheng@ymail.com

a controllable way. It has been reported that homogeneously aligned discotic columns can grow on poly(tetrafluororethylene) thin film which is coated onto substrate using friction method [12], or can be manipulated into a layer of discotic compound using a polarized infrared laser light [13]. Mouthuy et al. showed that a uniaxial alignment of the columnar mesophase was obtained in nano-grooves that were etched into the surface of an oxidized silicon wafer [14].

Recently, we produced microtrenches on substrates, and studied the molecular stacking of discotic molecules on the substrate. We demonstrate here that the discotic molecules in the trenches can assemble into uniaxially aligned columns. The way that the discotic molecules anchor on the walls of trenches and the overall orientation of the columns are determined by the energetic conditions of the walls. We show that the orientational direction of the columns can be controlled to align either parallel or perpendicular to the wall of the primary trenches using a set of properly designed controlling trenches.

2. Experimental

Microtrenches were produced on the substrates using conventional photolithography. For this purpose, a layer of negative photoresist SU8 (Gersteltec Sarl) was spin-coated onto a glass plate of dimension 25×25 mm^2. The photoresist layer was masked, exposed to an I-line (365 nm) ultraviolet illumination then developed. The portion of the photoresist that was exposed to light became insoluble to the photoresist developer, and remained on the substrate, whereas the unexposed portion of the photoresist was dissolved by the developer, and washed away. The pattern of the photoresist remained on the substrate is determined by the mask. In the present study, we considered the substrates with parallel trenches on the surfaces. Therefore, masks comprised parallel UV-transparent stripes were used. As the unexposed part of the photoresist layer will be washed away, the depth of the trenches is equal to the thickness of the photoresist layer, which can be determined by adjusting the spin speed of the spin-coater. In the present study, the depth of the microtrenches was set at 6 mm. In order to determine the surface energetic state of the photoresist, the surface free energy of a flat photoresist layer was measured using the sessile liquid drop method, and the measurement was performed using a DSA100 (Krüss) surface tension meter.

The discotic compound used was triphenylene (Fluka). The chemical structure of the discotic compound is shown in Figure 1. The discotic compound solution, with 5 wt% triphenylene dissolved in tetrahydrofuran (THF), was drop-coated onto the substrate and spread into the microtrenches. The sample was left at room temperature for a few hours to allow solvent to evaporate. A thermal anneal of the sample was carried out in order to drive discotic molecules to reorient. In the present study, all samples were thermally annealed at a temperature of 220°C (which is higher than the 210°C melting point of the compound). The temperature of the sample was controlled using a Linkam TMS94 temperature system (Linkam Scientific Instruments Ltd). The configuration of the discotic molecules and the orientation of the discotic columns in the sample were examined using a polarizing optical microscope (POM) (Axioskop40, ZEISS).

3. Results and Discussion

Regular parallel microtrenches, with 50% duty cycle were produced on the substrate. Molecular stacking of triphenylene molecules in parallel microtrenches was observed first. It was confirmed by POM examination that, initially, the tryphenylene molecules in the

Downloaded by [Moskow State Univ Bibliote] at 12:20 15 April 2012

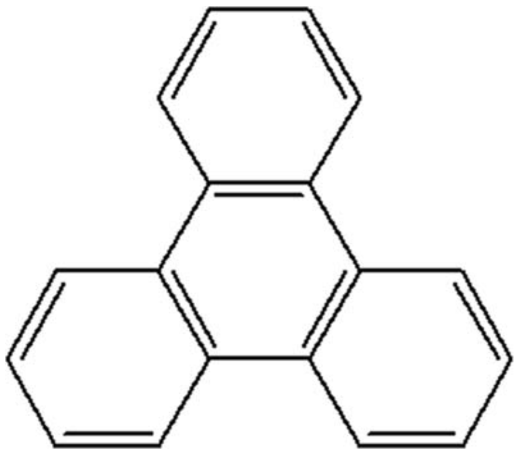


Figure 1. Molecular structure of triphenylene.

trenches were unaligned. A thermal annealing process will help the discotic molecules to assemble into an ordered structure. Figure 2 shows an image of a thermally annealed sample whose substrate consists of 20 mm-wide trenches on a 40 mm pitch. The trenches filled with the discotic molecules exhibited a uniform optical texture. When the sample was rotated in the POM, the appearance of the trenches filled with discotic molecules became dark (Figure 2a) and bright (Figure 2b) alternately as the azimuthal direction of the trenches varied. This indicates a homogeneous alignment of the discotic columns. While it can be used to decide the type of molecular alignment, the rotating sample in the POM cannot be used to distinguish in which direction the discotic columns lie as the columns oriented in either parallel to, or perpendicular to, the trenches may provide exactly the same optical result.

The orientation of the discotic columns was determined using a phase compensation technique in which a phase compensator is inserted into the optical path of the POM

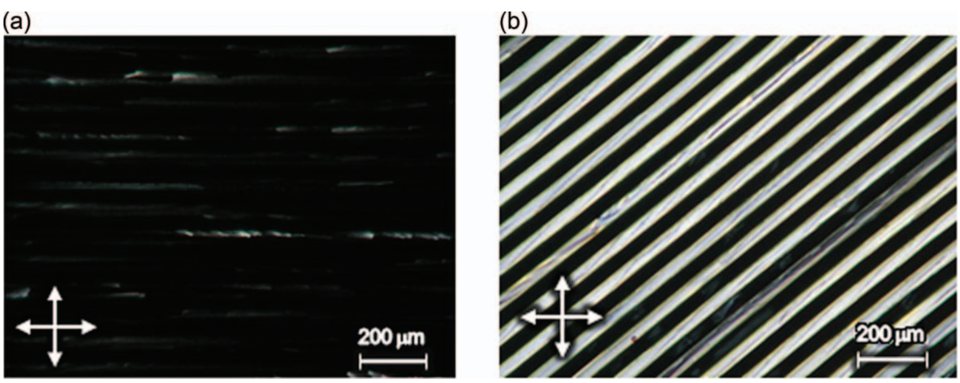


Figure 2. Optical appearances of triphenylene confined in microtrenches when the trenches aligned (a) parallel to and (b) to make 45° against the axis of the polarizer of the polarizing microscope, respectively. The white crossed arrow bars denote the orientations of the polarizer and analyzer of the microscope.

Downloaded by [Moskow State Univ Bibliote] at 12:20 15 April 2012

and a color pattern of the sample arises as a result of the interference of the light beams propagated through the sample [15]. With the optical axis defined to be parallel to the normal to the disc face of the molecule, most discotic molecules possess a negative optical birefringence. In the present study, the compensator was adjusted so that, when the optical axis of the discotic columns (i.e., the slow axis of the discotic columns) was parallel to the slow axis of the compensator, the long-wavelength light beams were transmit, whereas those of short wavelength were cancelled out by destructive interference between the two orthogonal linearly polarized components of the incident light. In the case described, the sample appears yellowish to reddish when the discotic columns are aligned parallel to the slow axis of the compensator. The main photomicrograph part of Figure 3 shows the interference color of the sample comprising parallel microtrenches. The discotic columns confined within the trenches are thus verified to be aligned parallel to the trenches as shown in the bottom drawn part of Figure 3.

In general, the way of the anchoring of the discotic molecules and the orientation of the discotic columns on a surface are determined by the energetic states at the interface created by the discotic molecules and other media. The discotic molecules normally reside in the face-on anchoring arrangement, i.e., with the disc-faces towards the surface, on a high surface free energy substrate, or in the edge-on anchoring arrangement with their edges in contacting with the substrates with low surface free energy [16]. The SU8 photoresist layers used in the present study were found to possess a surface free energy 39.96 mJ/m^2. The fact that the discotic columns are aligned parallel to the trenches indicates that the triphenylene molecules are stacking with the edge-on anchoring at the photoresist walls to satisfy the energetic conditions at the photoresist walls and at the interface with air. A complimentary case can be seen in [14], in which Mouthuy et al. showed that phthalocyanine molecules confined in trenches etched into an oxidized silicon wafer adopted a planar alignment with

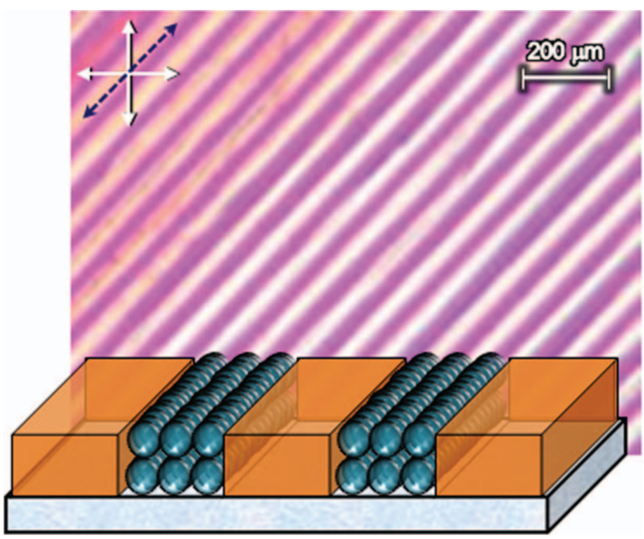


Figure 3. Interference color pattern of the triphenylene confined in the microtrenches. The dashed black arrow bar denotes the direction of the slow axis of the phase compensator inserted into the optical path of the microscope. The picture inserted describes schematically the orientation of the discotic columns in the trenches.

Downloaded by [Moskow State Univ Bibliote] at 12:20 15 April 2012

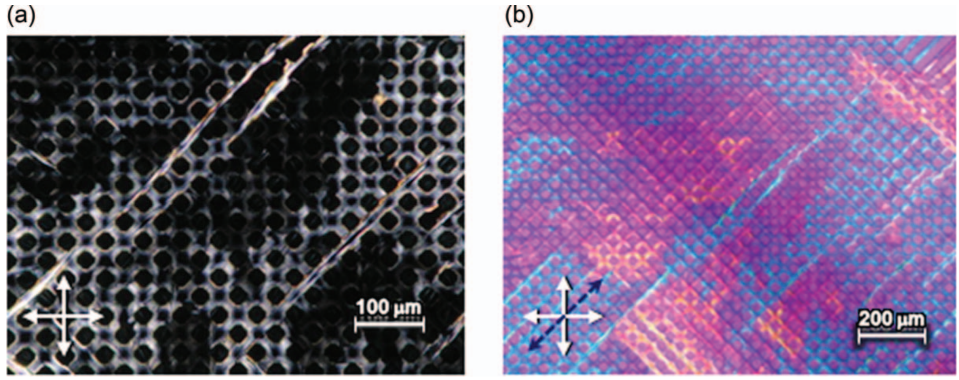


Figure 4. (a) The image of a sample comprised two mutually orthogonal sets of trenches with the same trench width and the same spatial period, and (b) the interference color pattern of the sample.

Downloaded by [Moskow State Univ Bibliote] at 12:20 15 April 2012

the discotic molecules in the face-on anchoring at the vertical oxidized silicon walls whose surface free energy (47.07 mJ/m^2) is higher than that of SU8 walls.

A second set of equidistant microtrenches, named the control trenches, were added, and set to be perpendicular to the original trenches. When the topology of both sets of trenches is the same, the two sets of trenches impose the same actions on the discotic molecules. As they are mutually orthogonal, the orientation-effects imposed by the two sets of the trenches on the molecules conflict, and cause chaos in the molecular stacking leading to uncertainty in the orientation of the columns. Figure 4 shows images of a sample comprised two mutually orthogonal sets of trenches with the same topology. The non-uniformity in the appearance of the sample in the POM, as illustrated in Figure 4a, indicates the incident light was blocked in some regions but manage to pass through in others. The pattern of the interference color of the sample (Figure 4b) clearly shows that the orientation of the discotic columns is different from one region to another.

The width of the control trenches was then reduced to be significantly smaller than that of the primary trenches. Figure 5a shows the photomicrograph of a sample in which a set of 3 mm-wide control trenches were added. The uniform optical texture indicates that uniaxial orientation of the discotic columns has been achieved. The discotic columns are in homogeneous alignment as confirmed by POM examination. The interference color pattern shown in Figure 5b indicates that the columns orient along the control trenches, i.e. perpendicular to the primary trenches (Figure 5c).

Another parameter that should be taken into account is the spatial distribution of the control trenches. A sample was prepared to have 20 mm wide trenches in both primary and control sets. The primary trenches were on a 40 mm pitch whereas the pitch of the control trenches was set to be 120 mm, i.e. six times of its width. The discotic columns assembled in the trench network were found to align homogeneously in the primary trenches, and to orient parallel to the primary trenches (Figure 6a). The alignment with discotic columns oriented parallel to the trenches was maintained even when the width of the control trenches was increased to be greater than that of the primary trenches, provided that the pitch of the control trenches was maintained at six times their width. This can be confirmed by the interference color pattern shown in Figure 6b, which was taken from a sample, in which the control set consists of 50 mm wide trenches distributed in a 300 mm pitch. A schematic drawing of the alignment of the discotic columns is shown in Figure 6c. Setting the pitch

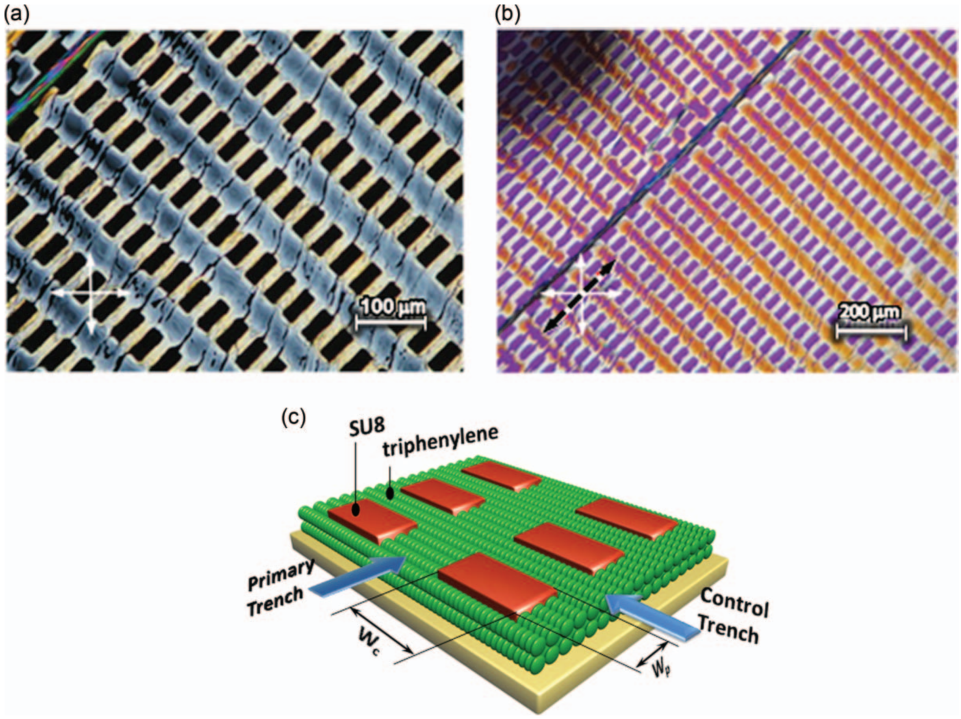


Figure 5. (a) The image of triphenylene molecules confined in the two sets of microtrenches. A set of 3 mm-wide trenches are added to control the prime trenches whose width is 20 mm. (b) The interference-color pattern of the sample. The dashed black arrow bar denotes the direction of the slow axis of the compensator. (c) Schematic drawing of the alignment of discotic columns in the trenches. In the case of $W_p < W_c$, the discotic columns align perpendicular to primary trenches.

of the control trench at six times its width was an arbitrary choice in the present study. Although it has not yet been verified, we suspect whether there is a critical distance that can be used for the control trench to regulate the orientation of the discotic columns assembling in the primary trenches.

To achieve a comprehensive elucidation for the assembly of the discotic molecules and the orientation of the discotic columns in the microtrenches, many parameters, such as the elastic characters of the discotic compound, intro- and inter-molecular actions, respective surface tensions at all interfaces and topologic structures of the surfaces etc., must be taken into account. Here we consider only the effects of the geometrical dimension of the microtrenches on the determination of orientational direction of the discotic columns. For convenience, we define the section of the wall of a control trench cut off by the adjacent two primary trenches as the unit control wall W_c, and that of a primary trench cut off by the adjacent two control trenches as the unit primary wall W_p. From the above observations, it can be seen that when the pitch of the control trenches is smaller than that of the primary trenches, as shown in Figure 5, the length of W_c is greater than that of W_p, and the discotic columns will align perpendicular to the primary trenches, i.e., parallel to the control trenches. When the pitch of the control trenches is greater than that of the primary trenches, i.e., $W_p > W_c$, the orientation of the discotic columns is parallel to the primary trenches, and the orientational configuration will not change even if the width

Downloaded by [Moskow State Univ Bibliote] at 12:20 15 April 2012

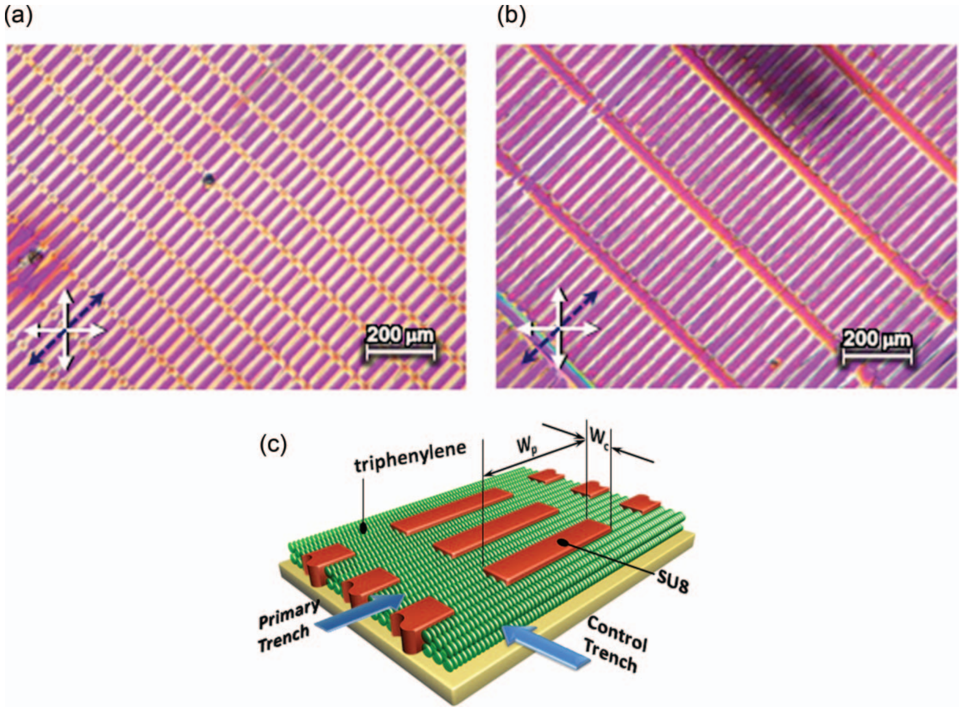


Figure 6. The interference-color patterns of samples comprised control trenches whose widths are (a) 20 mm and (b) 50 mm, respectively. The pitches of the control trenches in respective samples are set to be six times the widths of the respective control trenches. In both samples, the width of the primary trench is 20 mm. (c) Schematic drawing of the alignment of discotic columns in the trenches. In the case of $W_p > W_c$, the discotic columns align parallel to primary trenches.

of the control trenches is much greater than that of the primary trenches (cf. Figure 6). Without distinguishing between the primary and the control trenches, the samples shown in Figs. 5 and 6 can be thought to be identical with respect to a 90° rotation (cf. Figs. 5c and 6c). Consequently, the topological structure of the substrate plays an important role in determining the discotic column alignment. These arguments can be summarized as: for discotic molecules assembled in the trench-network system, the way that the discotic molecules anchor at the surfaces is determined by the surface energetic state of the walls, and the alignment of the discotic columns is determined by the topological structure of the trenches.

4. Conclusions and Perspectives

Microtrenches produced on the surface of a substrate can be used to regulate the assembly of discotic molecules. In the microtrenches with low surface energetic SU8 walls, triphenylene columns are aligned parallel to the trenches, with the discotic molecules anchored with the edge-on arrangement at the vertical walls. The orientational direction of the discotic columns can be controlled by adding an extra set of parallel microtrenches, which are set to be perpendicular to the primary trenches. When assembling in a network trenches formed by two sets mutually orthogonal trenches, the discotic columns were found to tend to stack

Downloaded by [Moskow State Univ Bibliote] at 12:20 15 April 2012

along the trenches with longer walls. By adjusting the pitch of one set of the trenches, the orientation of the discotic columns in another set of trenches can be tuned to align either perpendicular or parallel to the vertical walls. The technique provides a simple and effective way to achieve homogeneous alignment of discotic materials, and is expected to be used in fabricating discotic molecular wires. Moreover, by properly modifying the topological structure of the controlling trenches, it is possible to have an alignment template manipulated into the surface to locally controlling the alignment of discotic columns. Such a technique would be particularly useful for organic semiconductor devices that require a local-planar-alignment of discotic columns.

Acknowledgment

The authors acknowledge the financial support from the National Science Council of Taiwan (NSC992221E110056).

References

[1] Percec, V., Glodde, M., Bera, T. K., Miura, Y., Shiyanovskaya, I., Singer, K. D., Balagurusamy, V. S. K., Heiney, P. A., Schnell, I., Rapp, A., Spiess, H.-W., Hudson, S. D., & Duan, H. (2002). *Nature*, *417*, 384.
[2] Adam, D., Schuhmacher, P., Simmerer, J., Häussling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., & Haarer, D. (1994). *Nature*, *371*, 141.
[3] Chandrasekhar, S., & Balagurusamy, V. S. K. (2002). *Proc. R. Soc. London, Ser. A*, *458*, 1783.
[4] Furumi, S., Janietz, D., Kidowaki, M., Nakagawa, M., Morino, S., Stumpe, J., & Ichinmura, K. (2001). *Chem. Mater.*, *13*, 1434.
[5] Benning, S. A., Oesterhaus, R., & Kitzerow, H.-S. (2004). *Liq. Cryst.*, *31*, 201.
[6] Schmidt-Mende, L., Fechtenkotter, A., Müllen, K., Moons, E., Friend, R., & Mackenzie, J. D. (2001). *Science*, *293*, 1119.
[7] L. Schmidt-Mende, Watson, M., Müllen, K., & Friend, R. H. (2003). *Mol. Cryst. Liq. Cryst.*, *396*, 73.
[8] Christ, T., Glüsen, B., Greiner, A., Kettner, A., Sander, R., Stümpflen, V., Tsukruk, V. V., & Wendorff, J. H. (1997). *Adv. Mater.*, *9*, 48.
[9] Cocchi, M., Virgili, D., Fattori, V., Willians, J. A. G., & Kalinowski, J. (2007). *Appl. Phys. Lett.*, *90*, 023506.
[10] Dyreklev, P., Gustafsson, G., Inganäs, O., & Stubb, H. (1992). *Solid State Commun.*, *82*, 317.
[11] Sirringhaus, H., Wilson, R. J., Friend, R. H., Inbasekaran, M., Wu, W., Woo, E. P., Grell, M., & Bradley, D. D. (2000). *Appl. Phys. Lett.*, *77*, 406.
[12] Wittmann, J. C., & Smith, P. (1991). *Nature*, *352*, 414.
[13] Monobe, H., Kiyohara, K., Terasawa, N., Heya, M., Awazu, K., & Shimizu, Y. (2003). *Adv. Funct. Mater.*, *13*, 919.
[14] Mouthuy, P. O., Melinte, S., Geerts, Y. H., & Jonas, A. M. (2007). *Nano Lett.*, *7*, 2627.
[15] Hecht, E. (2006). *Optics*, 4th Ed, Addison Wesley, San Francisco, USA.
[16] Zheng, W., Hu, Y.-T., Chian, C. Y., & Ong, C. W. (2010). *Int. J. Mol. Sci.*, *11*, 943.

Downloaded by [Moskow State Univ Bibliote] at 12:20 15 April 2012