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Submicron-scale liquid crystal photo-alignment

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In this article, we disclose a method to achieve submicron-scale resolution for liquid crystals by photo-alignment of the sulfonic azo dye (SD1) layer. The interference pattern produced by Lloyd's mirror has been used to produce two alignment domains. The easy axes in these alignment domains are mutually perpendicular to each other, in the plane of the substrate. The two-step alignment process, *i.e.* the first uniform alignment and the second alignment by interference pattern, provides resolution up to 105 nm for the liquid crystal alignment domain size that typically corresponds to the existing experimental limits. Optical methods such as optical microscopy and diffraction in the transmissive and reflective regimes have been used to analyze the fabricated gratings.

Introduction

The research and development in the field of high-resolution liquid crystal (LC) structures with submicron and nanometer domain size are widely developed in recent times. These structures have a wide range of uses, from two-dimensional nano-gratings to three-dimensional photonic crystals as well as many more applications. Polymer thin films with high-resolution topology with controlled period and height of the vertical groove profile are able to produce a broad range of optical elements.[1] Soft materials including LC molecules are also in high demand for nano-electronics.[2] It also became possible to create a fiber structures based on LCs for nano-electronics and photonics.[3,4] Recently, Yoona *et al.* have demonstrated the alignment of lyotropic molecules such as DNA, RNA *etc.* in micro channels which is vital for various bio-medical studies.[5] Tunable filters and retarders based on patterned alignment have also been developed.[6–8] The rapidly growing field of LC photonic crystals for 3D structures with a given distribution of optical properties that provides control of the optical characteristics of light at the nano-scale is another important application.[9,10] The ability of LCs to flow and fill nano-gaps has facilitated the creation of 2D and 3D tunable photonic crystal devices as well as structures made of porous materials.[6] In porous LCs with a submicron diameter, molecules are assumed to follow submicron-scale alignment.[11] Thus nanoscale LC alignment is the real time demand of current and modern photonic devices.

Several methods to realize the high-resolution alignment for LCs have been proposed. The most commonly used method is nano-imprinting.[12,13] This scheme offers resolution up to 50 nm.[14] Another method is based on the directional peeling effect, which could provide 100 nm of the pattern size.[15] On the other hand, extreme ultraviolet lithography can be used to achieve very high resolution up to 29 nm.[16] A method of 2-beam interference has been used to obtain LC gratings.[17] Moreover, 3-beam interference through a mask has been proposed to develop single-exposure lithography fabrication of photonic-crystal structures.[18,19] In another approach, a new kind of nano-structured alignment based on nano-imprinting and plasma etching has been proposed.[20] Such an alignment surface is capable of generating arbitrary pre-tilt angles for the LCs. Moreover, a photo-aligned non uniform pre-tilt angle with limited resolution was used to produce the LC lens.[21] The method of nano-rubbing which uses the stylus of an atomic force microscope has recently been recognized as an impressive technology for the fabrication of novel micro and nano structured LC electro-optic devices.[22] Special self-assembled substrate patterns were used to generate nematic domains with certain molecular orientations.[23] The holographic formation of LC polymers incorporating azobenzene units has also been extensively investigated, aiming primarily at high-density optical memory.[24]

Among all of the above-mentioned methods, the most developed and commonly used method of nano-imprinting

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could produce the highest resolution patterns, but it is extremely dependent on the photo-resist and mask quality. Moreover, fabrication of such a high-resolution stamp is expensive. However, photo-alignment could be the better and cheaper option to fabricate nano-photonics and optical components.

Photo-alignment includes four popular approaches *i.e.* photo-crosslinking,[25–27] photo-destruction,[28] photo-isomerisation,[29] photo-reorientation and the diffusion mechanism.[30] The photo-reorientation method involving the sulfonic azo dye (SD1) molecules shown in Fig. 2. The anchoring energy for this material is $\sim 10^{-4}$ J m^{-2} which is comparable with other photo-alignment and alternative alignment materials. Moreover, the photo-reorientation method requires the smallest energy of $\sim$0.3 to 0.8 J cm^{-2} to obtain sufficiently high anchoring energy, while other methods require relatively higher amounts of energy, in the range of 2–9 J cm^{-2}.[31] Furthermore, the photo-reorientation method is eco-friendly because SD1 molecules can be aligned using visible blue light at 400–450 nm.[32] While for other schemes, UV or deep UV light is required for exposure. Another feature of the diffusion mechanism is to change the orientation of the easy axis several times by sequential energy exposures.[27,33] This rewriting ability of the photo-reorientation method provides an opportunity to precisely modify the pre-alignment and realize the multi alignment domain on the same substrate by several exposure steps and to achieve submicron-scale resolution.

In this article, we disclosed a method to obtain submicron-scale high-resolution structures using a diffusion mechanism of photo-alignment. The main objective is to determine the maximum resolution (*i.e.* minimum size of the alignment domain) that can be obtained using the photo-alignment, for which the sulfonic azo dye (SD1) are capable of maintaining the preferred orientation of easy axis with sufficiently high anchoring energy, wherein the LC molecules have different easy axis directions in different alignment domains.

Experimental

Several methods have been proposed to achieve high resolution LC alignment. Two-beam interference pattern is one of them, where the alignment layer is exposed by the interference pattern of the two beams.[18]

Interfering beams can be both linearly or elliptically polarized, which can produce different interference patterns.[34] The period size depends on the angle between the interfering beams which is governed by the simple interference formula ($d = \lambda/2\sin\theta$). Thus, the theoretical limit of the minimum period for this method is $\lambda/2$, however experimentally it is almost impossible to achieve this limit and the reason has been discussed later in the article. The 2-beam interference was used by Lu *et al.* in the framework of the diffusion mechanism to obtain LC gratings where they successfully achieved a period size of $\sim$1.67 μm .[17]

In another approach, three beam or multi-beam interference has been proposed to construct two-dimensional structures with complex molecular orientations and different domain shapes.[35] Another possibility is to combine three-beam interference with mask projection on the specimen to manipulate the alignment domains in two-dimensional space.[18]

All of these methods based on two or multiple beam interference thus impose few constraints to achieve a high-resolution (<1 μm pitch) interference pattern. The presence of temperature gradients in the environment including vibrations in the air and surroundings, leads to spatial and temporal variations of the refractive index in the medium. This influences the propagation parameters through the environment and causes imbalance of the interfering beam phases and consequently deteriorates the interference pattern. A stabilizer can be used to avoid this problem but to get good anchoring energy for the photo-alignment layer, exposure energy doses must be in the order of a few J cm^{-2}, which requires a long exposure time. For such stabilizers, it is very difficult to control the surrounding conditions for long times, which is also inefficient for large-scale production. As a result, the scheme of two-beam interference has to be modified.

Therefore, for our interference experiments, we have chosen the Lloyd's mirror scheme.[19,36] Lloyd's mirror consists of two plates connected to each other at right angles. The mirror is attached to one of the plates, and the SD1 coated sample (pre-aligned with one preferred easy axis) was fixed on to the other plate (Fig. 1).

A laser beam passes through the beam expander and goes to the Lloyd's mirror. A part of the beam that hits the mirror is reflected and interferes with the second part of the beam on the PA substrate. Thus, because of one beam, this approach significantly reduces the area of the beam separation and, consequently the phase imbalance that occurs as a result of vibration and temperature gradients is drastically reduced. By changing the incident angle, for the impinging light to the Lloyd's mirror, it is possible to reduce the pitch of the interference pattern and consequently increase the resolution of the alignment. The minimum possible pitch for the interference pattern by this approach is $\lambda/2$ and because of the two spans in one period, a pre-aligned SD1 substrate can be exposed by this interference pattern to achieve the alignment domain size of $\lambda/4$ with mutually perpendicular easy axes in two alignment domains. The laser of $\lambda = 405$ nm has been used in these

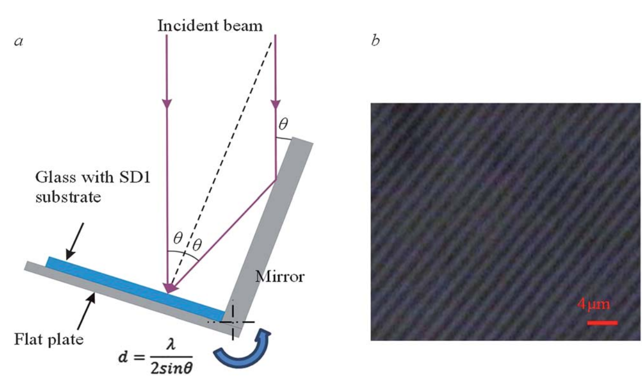

Fig. 1 (a) Schematics of the exposure system based on Lloyd's mirror. (b) Optical micro-photograph of the LC grating with 2 micron pitch. The marker size is 4 μm.

experiments and thus the minimum possible size of the alignment domain is 101.25 nm.

The method of sample fabrication is as follows: 0.5% SD1 solution in *N*,*N*-dimethylformamide (DMF) was spin-coated on the glass substrate (3000 RPS, 30 s) to create a uniform layer. Then, the substrate was heated to evaporate the excess DMF for 5 minutes at a temperature of 100 °C. Afterwards, the first planar alignment was made by illuminating the substrate by linearly polarized light, with a wavelength of 405 nm for 45 seconds, to provide the first preferred direction (Fig. 2).

In the second exposure step, the same substrate has been exposed by the interference pattern by the Lloyd's mirror. The plane of the polarization of the exposing light has been set perpendicular to the light used in the first step. Therefore, the molecules at the interference maxima re-orient in a perpendicular direction to their initial direction. Thus two alignment domains, with mutually perpendicular easy axis, have been defined on the SD1 coated substrate. The ability of the SD1 to rewrite the alignment direction with another exposure gives us an opportunity to achieve submicron-scale resolution. As the proposed method includes two step exposure, the first by direct exposure and the second exposure by the interference pattern, it is critically important that the minima is sufficiently dark.

After defining these photo-alignment domains, the substrate has been coated with the 5–10% wt/wt solution of LC polymer (LCP) ULC17 (from DIC) in propylene glycol monomethyl ether acetate (PGEMA) followed by thermal annealing (at 80 °C for 5 min) and UV exposure to fix the LCP layer. The LCP molecules simply follow the easy axis in different alignment domains and thus generate the periodic distribution of the indexes and consequently the diffraction.

Analysis of quality

The analysis of such a submicron-scale aligned domain is equally difficult as fabrication. Different methods for the analysis and their limitation have been discussed in this section and both optical and non-optical methods have been used to analyze the optical quality of the produced structure. The optical methods include optical microscopy and diffraction in the transmissive and reflective regime, while non-optical methods include atomic force microscopy.

Polarizing optical microscopy can be used to analyze the periodic distribution of refractive index in the LC gratings. The texture in Fig. 1(b) is one simple example, which shows different transmittance in two alignment domains. However, this method is limited, usually, to analyze the domain size up to ~1 μm.

Other possibility is scanning microscopy that could be used for the analysis of the submicron alignment domain size. The surface topology analysis and electric force microscopy mode at the surface can be used. However, the surface topology in both domains is the same (Fig. 2) thus, the measurement from the atomic force microscope does not provide any vital information. Moreover the SD1 molecules in two alignment domains are mutually perpendicular in the same plane and thus the vertical electrostatic gradient does not vary from domain to domain and therefore electric force microscopy is also not capable of analyzing the submicron structures.

Thus, for the analysis of such structures with submicron resolution, diffraction in the transmission regime has been used. The diffraction profile for the diffraction in the transmission regimes is expressed by:

$$d\sin\theta = m\lambda, \tag{1}$$

where d is grating pitch and θ is angle of deflection of the diffracted beam. Thus the diffraction in the transmission regime is limited to $d \geq \lambda$ and no diffraction appears for $d < \lambda$. Thus, the minimum period when diffraction could be observed is equal to the wavelength of the analyzing beam, in our case it is 405 nm.

For the analysis of submicron scale alignment for $d < \lambda$, the diffraction in the reflection regime has been used (Fig. 4). The reflective type diffraction profile can be defined as:

$$d(\sin\theta + \sin\theta^i) = m\lambda, \tag{2}$$

where θ is incident angle of light beam and θ^i is the angle of the first order diffracted beam with the normal of the surface. For the reflective regime, the minimum period size when the reflection diffraction is visible is $d \geq \lambda/2$, and thus the limit for the minimum domain size that can be analyzed by this approach is $\sim\lambda/4$ or 101.25 nm in present case.

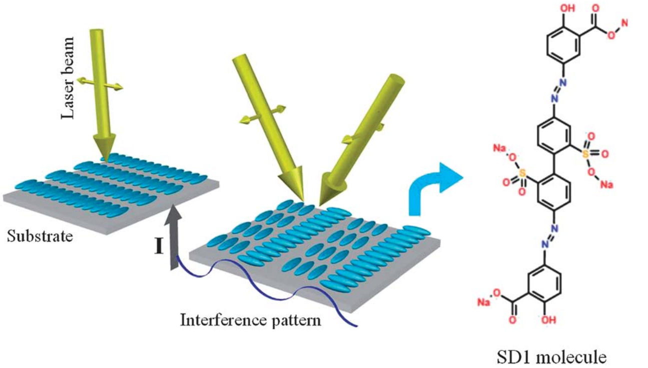

Fig. 2 Two stage exposure procedure for the fabrication of the gratings with submicron pitch. The right-hand insertion represents the molecular structure of the sulfonic azo dye SD1.

Results

As described above, we have achieved a domain size of 105 nm using the Lloyd's mirror interference without any problems. Gratings with period > 2–1.5 μm were analyzed using a polarizing microscope (Fig. 1). But for gratings with 405 nm < d < 1 μm were analyzed by diffraction pattern analysis in the transmission regime (Fig. 3).

A good diffraction pattern has been observed until d = 405 nm. The solid legends in Fig. 3 represent the experimentally measured pitch achieved for different exposing interference angles, while the red line corresponds to the theoretical fit. As seen from the Fig. 3, the experimental results are in good

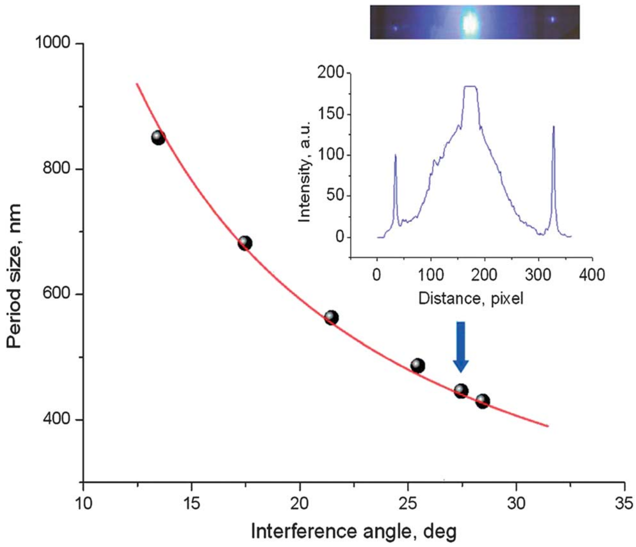

Fig. 3 The solid circles show the experimentally measured period size for different interference angles for diffraction in the transmission regime where the red line describes theoretical fitting for the period size according to eqn (1). The inset represents the diffraction pattern for $d = 444$ nm and the corresponding intensity profile.

agreement with the theory. The diffraction patterns and respective intensity profile for the $d = 444$ nm has been shown in the inset of the Fig. 3. It clearly confirms that we have achieved an alignment domain size of 202.5 nm which is already a breakthrough in the field. However, with the further increment in the θ, we can achieve an even smaller domain size but the diffraction in the transmission regime is not capable of analyzing such high resolution submicron structures.

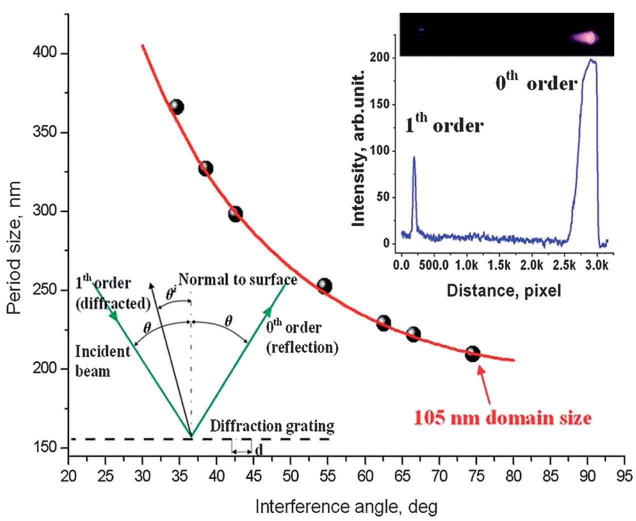

Fig. 4 The solid circles show the experimentally measured period size for different interference angles for diffraction in the reflective regimes, where the red line describes theoretical fitting for the period size according to eqn (2). The inset represents the 1st order diffracted beam image for $d = 229$ nm and corresponding intensity profile.

Therefore, the higher resolution grating has been analyzed by diffraction in the reflective regime.

Fig. 4 shows the experimentally measured pitch for the diffraction pattern in the reflective regime depending on the interference angle. The solid legends represent the experimental data while the red line is the theoretical fit of eqn (2), which matches well with the experimental results. As seen from the figure, the size of the smallest pitch is 210 nm which is very close to the resolution analysis limit of diffraction in the reflective regime (*i.e.* ~202 nm).

Herein, the limit of optical analysis is comparable with the fabrication limit of the method, *i.e.* the pitch of the interference pattern generated by Lloyd's mirror. The inset in the bottom left of the Fig. 4 represents the conceptual presentation of the diffraction in the reflective regime. Whereas the insertion in the right up corner represents the diffraction pattern in the reflection regime and the corresponding intensity profile for one of the gratings with $d = 229$ nm.

Thus, resolution close to the experimental regime has been achieved but the optical quality is another important factor for such elements. Therefore, the optical and alignment quality of the grating has been analyzed by plotting the diffraction efficiency as a function of the grating period in Fig. 5. For the period size 900 nm, the diffraction efficiency for the first order is about 40%, which is close to the theoretical limits.[36,37] The diffraction efficiency decreases for a smaller period size which clearly concludes that the fill factor decreases for smaller periods. Nevertheless, for a period of 205 nm, the diffraction efficiency is ~15%. This smaller diffraction efficiency can be attributed to the smaller fill factor. In other words, the anchoring energy of the alignment domain for the second exposure is not enough to define the alignment domain boundaries for the bulk LCP layer. However, the anchoring energy of the SD1 strongly depends on the exposure energy which can be increased up to the optimum value.[8,32] Thus, the diffraction efficiency can be improved further by the

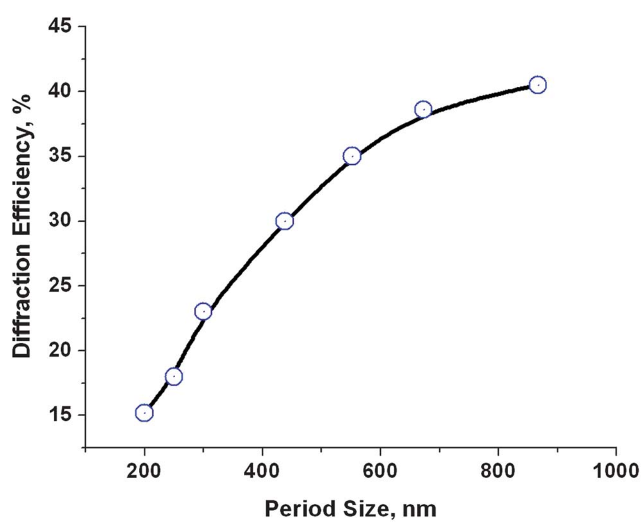

Fig. 5 The period size dependence of the diffraction efficiency in percent.

optimization of the exposure energy and anchoring energy for the second exposure.[32]

Conclusions

In conclusion, we intended to show the maximum possible resolution (*i.e.* minimum alignment domain size) for the photo-alignment of LCs. It is a well established fact that the existing methods are very expensive and involve very difficult fabrication procedures. We have disclosed a simpler and less expensive method to achieve the minimum domain size of 105 nm by photo-alignment of the sulfonic dye SD1. A two step alignment involving Lloyd's mirror interference technology for the second step has been used to achieve this high resolution. The theoretical limit for the minimum period of the interference pattern is $\lambda/2$ and the 2-step alignment provides the opportunity to achieve a domain size equal to $\lambda/4$. Here λ corresponds to the wavelength of the exposing light, in the present case it is 405 nm, thus the theoretical limit of the system is ~101 nm.

Analysis of the thus achieved resolution is another challenge. Because the surface and electrical (Fig. 2) topology in both of the alignment domains with mutually perpendicular easy axis is the same, AFM analysis is incapable of providing any vital information about fabricated the submicron-structure. The only possibility until now is the diffraction in the transmissive and reflective regimes. The limit for the pitch in the transmissive diffraction regime is λ whereas, for the reflective regime it is $\lambda/2$. Therefore, in our case, one can analyze the minimum domain size of ~100 nm.

Therefore, the results achieved in this article typically correspond to the theoretical limit for both fabrication and analysis. The experimental results are in good agreement with the theory and the method to achieve the higher resolution could align LCs up to a resolution of 100 nm.

Thickness of the LCP layer is also a crucial parameter to find the real resolution limit and to align a thicker LCP layer, higher exposure energy is required and could be optimized for different LCP thickness. Thus the proposed submicron-scale alignment domains can find applications in many current and modern photonic devices like photonic crystals,[9] high-resolution gratings,[18] patterned polarizer[38] *etc.* Moreover, the same setup can also be used to align and investigate properties of DNA, RNA and other lyotropic samples.

Furthermore, the SD1 shows some absorption even at 300 nm therefore it is possible to achieve an even higher resolution with a domain size of ~75 nm by exposing the SD1 substrate by polarized light of $\lambda = 300$ nm; however, analysis of such a high resolution could be an issue at this point of time.

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