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Polarization-Selective Patterning in an Anisotropic Smectic B Film

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Optical lithography is an important patterning technique that is almost exclusively based on the recording of a light intensity pattern in a light-sensitive material called photoresist.^[1] In this work, we show by polarization holography that the direction of the electric-field vector (or polarization state) of light can be used as additional tool for patterning by illumination of a polarization-selective liquid crystalline (LC) photoreactive material. The addition of this extra polarization-selective parameter is anticipated to further expand on the versatility of lithography, e.g., enabling patterning without masks, thus, omitting problems as diffraction at mask edges. Polarization-selectivity also offers the opportunity for patterning in the third dimension by means of 3D orientation patterns^[2] and the enhancement of the resolution of optical lithography by using longitudinal components in dedicated laser beams.^[3]

Liquid crystals in general are known to interact with the polarization state of light.^[4] A first example is the birefringence related to the anisotropy in polarizability which in general results in a high refractive index for polarized light parallel to the resulting common orientation direction (director) and a lower refractive index perpendicular to that.^[5] Related to this the state of polarization of transmitted light is altered when the director is under an angle with the net electrical field vector. Dye molecules with an anisotropic, and therefore dichroic nature, aligned in a liquid crystal have a more intense response to light polarized parallel to the director. This may result in an enhanced absorption of light,^[4] and enhanced fluorescence^[6] or even directionally controlled photomechanical responses.^[7] The polarization-selectivity of the LC photoreactive material arises from a rod-shaped dichroic photoinitiator (DPI) which mainly absorbs the polarization state of light that is along the long axis of this molecule.^[8,9] An example of a DPI is shown in Figure 1a. This material photodissociates into free-radical fragments when addressed with UV light with its electrical field vector parallel to the long axis of the molecule and is largely insensitive for light with its vector perpendicular to that. Achieving selectivity

toward a single polarization state requires uniaxial alignment of this initiator which is accomplished by coaligning it in a highly ordered reactive LC material. Previous studies have shown that the polarization-selectivity of the LC photoreactive mixture largely depends on the degree of order of the LC material.^[8,9] A preferred liquid crystal phase for our purpose is the smectic B where the rod-shaped monomer molecules and its rod-shaped DPI are densely hexagonally packed in a layered organization. The acrylate molecules we used to create a polymerizable liquid crystal mixture (LCM) are shown in Figure 1a. The monoacrylate provides the smectic B phase. The diacrylate, added only in low concentration, provides crosslinking during polymerization and is responsible for the insolubility of the formed polymer structures. The alignment of LCs can be controlled by the application of alignment layers, surfactants, shear, or an electric or magnetic field.^[10] The absorption of the DPI depends on its alignment with respect to polarization axis of linearly polarized light and on the in-plane distribution function of the axis of the transition moment of the DPI. The absorbed intensity is highest for photoinitiator molecules that are aligned parallel to the polarization axis of light which also provides the highest concentration of free radicals formed per unit of time under polarized illumination. The free radicals induce polymerization and network formation which insolubilize the areas with their orientation closest to the polarization axis faster than the areas with their orientation perpendicular to that. Kinetic parameters like sensitivity of the photoinitiator, polymerization rate, and exposure determine the area that becomes insoluble. The areas with low conversion can be removed by a solvent which makes the system employable as a negative photoresist.

In order to show that the polarization state of light can be used for structuring requires a polarized light pattern.^[11,12] We have chosen to create this pattern by means of polarization holography. Holography or interference lithography is a fabrication method for a myriad of applications such as nanophotonics, data storage, and filtration.^[13,14] It is an attractive and cheap technique which offers fast nanometer-scale resolution patterning on a relatively large scale (cm^{-2}) without the application of a mask.^[13–15] Holography is based on the interference of two or more coherent laser beams where the interference results in the modulation of the intensity and/or polarization which can be recorded in a photoresist.

Different intensity or polarization patterns can be produced depending on the polarization and intensity of the interfering beams.^[12,16] Two beam polarization holography employs the interference of two orthogonal circularly polarized (left- and right-handed) laser beams with equal intensities. This interference results in a 1D polarization pattern with pitch Λ where the intensity remains constant (Figure 1a). The pitch depends on the half-angle θ between the two interfering beams and

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Figure 1. a) Two-beam polarization holography where two orthogonally circularly polarized laser beams with wavelength λ interfere at angles of $+\theta$ and $-\theta$ to create a periodic pattern with pitch Λ . b) Polarization holography performed on monolithic planar aligned photoreactive material with liquid crystal mixture (LCM; gray) and dichroic photoinitiator (DPI; white). Polymerization will occur in areas where the polarization, indicated by the arrows, is predominantly parallel to the alignment (areas are marked blue). After exposure, a postexposure bake (PEB) is applied and subsequently the cell is opened and etched with acetone. c) Optical images of the uniaxial-planar aligned photoreactive material between crossed polarizers with the director 0° or 45° rotated relatively to one of the polarizers. The white arrows indicate the alignment direction while the red arrows indicated the orientation of the crossed polarizers.

the wavelength λ . To record this polarization pattern into the LC photoreactive material, a monolithic planar alignment is required (Figure 1b). Due to the polarization-selectivity of the aligned photoinitiator, a polymer network forms at the location where the polarization is parallel to the director. Removing the nonpolymerized area by a solvent results in a line grating. The required alignment of the LC monomers is established by means of an alignment layer coated on the glass substrate and subsequently rubbed with a cloth. A cell is made from two of these substrates facing each other kept at a constant distance by means of spherical spacers. The cell was filled with the monomer mixture through capillary action. The composition of the SmB photoreactive material and its phase behavior is described elsewhere.^[9] Figure 1c shows polarized optical microscopy (POM) images of the aligned LC between crossed polarizers. A dark and a bright state appears when the director is 0° or 45° rotated relative to the polarizers, respectively. At an angle of 45° the linear polarization state produced by the first polarizer changes to elliptically polarized light as the light passes through the photoreactive material as a result of the birefringence of the LC film. The second polarizer placed orthogonal to the first polarizer only partially blocks the light and, therefore, a bright

colored state appears. The color is determined by the optical retardation and can be found in the second order region on the Michel-Lévy interference color chart where the product of thickness and birefringence is around 1000 nm.^[17] At an angle of 0° the polarization does not change passing through the material. Therefore, the light is fully blocked by the second polarizer resulting in a dark state. This result confirms the monolithic planar alignment of the photoreactive material.

After confirming the desired alignment, the photoreactive material was exposed with a polarization holographic pattern with a pitch of 6 μm . In Figure 2a, a POM image is shown of the material after illumination and postexposure bake (PEB). Straight colored lines appear parallel to the alignment, which indicates a change of the optical retardation in areas where the material is polymerized. The origin of the change in optical retardation, defined as the product of thickness t and birefringence Δn , is twofold. The sample is subjected to polymerization shrinkage decreasing the path length t of transmitted light. But more importantly the intrinsic Δn is changed by a small reduction of the order parameter. The order parameter in these highly ordered systems is known to be reduced upon polymerization because of steric effects when the packing of molecules

Figure 2. a) Optical images between crossed polarizers of the photoreactive material after exposure with polarization holography and postexposure bake. The alignment of the liquid crystalline mixture is indicated by the arrow. b) The diffraction pattern of the photoreactive material in the SmB phase before and after polymerization where d_L is the layer spacing and d_i is the intermolecular distance. The order parameter S can be derived from the d_i signal according to the equation where $I(\theta)$ is the intensity distribution as a function of the azimuthal angle θ .

becomes higher due to an increase in density (polymerization shrinkage).^[5] This is confirmed by our X-ray diffraction (XRD) measurements. Figure 2b shows the XRD diffraction patterns of the photoreactive material before and after polymerization. There are two sets of diffraction patterns based on the molecular organization in the smectic B phase corresponding to the molecular layer spacing (d_L) and the intermolecular distance (d_i).^[18] Based on the d_i signal an order parameter S can be calculated according to the equation in Figure 2b,^[19] where $I(\theta)$ is the intensity distribution as a function of the azimuthal angle θ as defined in Figure 2b. The d_i signal broadens after polymerization which results in a decrease of the order parameter from 0.94 to 0.91. The corresponding decrease of the birefringence lead to the contrast in optical retardation lines observed in Figure 2a.

The lines have a pitch of 6 μm as set by the angle of the two interfering beams. This result validates the polarization-selectivity

of the photoreactive material. After the PEB, the cell is opened and the unpolymerized areas were removed by dissolving in acetone. The adhesion of the liquid crystalline polymer with the substrate is poor resulting in local detachment when the top substrate is removed as shown in Figure 3a–c. Because of poor adhesion also some pairing of neighboring lines can be observed. However, besides these shortcomings it can be seen that free-standing lines (Figure 3a,b) can be created with sharp walls (Figure 3c). The line width and standard deviation as measured from the SEM pictures is $3.78 \pm 0.07 \mu\text{m}$. With a sinusoidal intensity distribution with a pitch of 6 μm this means that the angle between the polarization axis of light and the orientation axis of the molecules at which still an insoluble polymer is formed is 57° . The effective intensity of absorbed UV light at this position is estimated to be 30% of the maximum intensity at the position where polarization and alignment are

Figure 3. a) Optical image between crossed polarizers of the photoreactive material after opening the cell and developing with acetone. b,c) Corresponding SEM images of the fabricated grating. The alignment of the liquid crystalline mixture is indicated by the arrow. d) The initial stage of the conversion of the reactive bonds during polymerization as a function of time of UV exposure with the polarization state of light parallel (//) and perpendicular (⊥) to the molecular alignment.^[9]

parallel. At this point, it should be noticed that these numbers depend on the exposure conditions such as time, intensity, and the presence of inhibitors. For example, a longer exposure will lead to a larger angle and corresponding larger line width. The observation of the formation of squared lines is remarkable as the polarization pattern rotates in a sinusoidal fashion (Figure 1b). The absence of a sinusoidal response points to a sharp contrast in sensitivity toward absorbed light during the holographic exposure. This is confirmed in the conversion dose response curve Figure 3d which shows the initial stage of the conversion of the reactive bonds of the photoreactive material upon polymerization as a function of the exposure time with polarized ultraviolet light.^[9] When the polarization state is parallel (//) to the monomer alignment the reaction directly sets in whereas when the polarization state is perpendicular ($\perp$), the reaction is delayed. The large inhibition period for perpendicular light is enhanced by the presence of inhibitors in the formulation which at low concentrations of free radicals prohibits polymerization but as soon as the free-radical concentration exceeds a critical value the photocrosslinking reaction starts with relatively high speed. In general, this highly nonlinear light-response of photoresists is a desired property for high-resolution lithographic applications.^[20]

To summarize, we have shown that the polarization state of light can be used as a parameter for optical lithography by exposing an aligned LC photoreactive material with a polarization pattern obtained by interference holography using orthogonally circularly polarized beams. The high-order parameter of the smectic B, taken over by the photosensitive dichroic chromophore, in combination with a low concentration of a free-radical scavenger, provides a high contrast. This is demonstrated by the formation of line structures with a squared cross section despite the polarization pattern is sinusoidal. We anticipate that after further optimization, especially with respect to the adhesive properties to the substrate, the developed lithographic material can be used for mask-less laser patterning by controlling the polarization state of the laser beam and for increased resolution of optical lithography reducing diffraction limitations.^[7]

Experimental Section

The composition and the phase transitions of the smectic B photoreactive material is described elsewhere.^[9] Monolithic planar alignment was achieved by sandwiching the material between two glass plates with a gap of $\approx 3 \pm 1 \mu\text{m}$ (cell) coated with two different alignment layers. One glass plate was coated with rubbed polyvinyl alcohol (PVA) while the other glass plate was coated with rubbed polyimide (JSR Micro AL-24101). Two different alignment layers were used in order to obtain the structures mainly adhering to a single glass plate after opening of the cell. The polymerized film adhered better to the PVA surface. The polyimide was spin coated on the glass substrates with a two-step program: 1000 rpm for 5 s and subsequently 5000 rpm for 30 s. In both steps the acceleration was 2000 rpm s^{-1} . After spin coating, the substrates were placed on a hotplate at 85°C for 1 min before being baked for 90 min in an oven set at 180°C . For the PVA layer, a 5 wt% PVA aqueous solution was spin coated on the glass at 2000 rpm for 30 s and with an acceleration of 500 rpm s^{-1} and subsequently baked at 90°C for 30 min. A cell was prepared by using glue glass spacers to control the thickness of the layer. The cell was filled through capillary action at

140°C and subsequently cooled down to room temperature. POM was performed with a Leica CTR 6000 microscope equipped with crossed polarizers; images were recorded with a Leica DFC420 C camera.

The XRD analyses were performed on samples sealed in a 1 mm glass capillary inside a custom-built heating stage equipped with a 1 Tesla permanent magnetic field to stimulate molecular alignment in the liquid crystal phases. The monomer mixture was heated with a rate of $30^\circ\text{C min}^{-1}$ to the isotropic phase first before being cooled down with $10^\circ\text{C min}^{-1}$. The monomer mixtures were analyzed upon cooling and were irradiated with a $1.54 \text{ \AA}$ GeniX-Cu ultralow divergence source. The diffraction patterns were recorded on a Pilatus 300K silicon pixel detector. Silver behenate was used for calibration.^[21]

The polarization holography setup is shown in Figure 1a. The intensity of the laser (Quanta-Ray Nd:Yag Lab-150 355 nm pulsed laser, 10 Hz, seeded) was regulated by a half-wave plate ($\lambda/2$). After the beam passed a polarizing beamsplitter, the reflected s-polarized beam passed a shutter and was reflected by a mirror to a beamsplitter after which the two beams passed through a quarter-wave plate. The light was converted to the left- and right-handed circularly polarized light, respectively. The sample was placed at a position where the two beams interfere and this location depends on the desired pitch determined by the grating equation (Figure 1a). Here, a pitch of $6 \mu\text{m}$ was created with a half angle θ of 1.7° between the two beams. The illumination was performed at ambient conditions. After exposure, the photoreactive film was heated for 1 min at 80°C , cooled back to room temperature, subsequently the cell was opened and the unpolymerized areas were etched with acetone for 5–10 s. The produced gratings were analyzed with POM and scanning electron microscopy (JEOL JSM 5600). For the latter analysis, a 40 nm thick gold layer was deposited on the grating.

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