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Flexible Structures Based on a Short Pitch Cholesteric Liquid Crystals

GIOVANNA PALERMO,[1] LUCIANO DE SIO,[2,*] AND CESARE UMETON[1]

[1]Department of Physics, and Centre of Excellence for the Study of Innovative Functional Materials, University of Calabria and NANOTEC-CNR, Unit in Cosenza, Arcavacata di Rende, Italy
[2]Beam Engineering for Advanced Measurements Company, Winter Park, Florida, USA

We report on the realization and characterization of electro-responsive and pressure sensitive polydimethylsiloxane (PDMS) conductive photonic structures combined with the reconfigurable properties of short pitch cholesteric liquid crystals (aligned in Grandjean configuration). By combining ion-implantation process and surface chemistry functionalization, we have overcome the insulating properties of PDMS and induced long range organization of cholesteric liquid crystals, thus controlling both diffraction and selective Bragg reflection of light by means of external perturbations (electric field, pressure). We have characterized our devices in terms of morphological, optical and electro-optical properties.

Keywords Liquid Crystals; Polymers; Diffraction Gratings; Optics

Introduction

Nanoscience and nanotechnology are interdisciplinary fields, involving physics, chemistry and materials science. At the nanoscale, the optical, electric and magnetic properties of materials change, allowing the realization of new functional materials with unique properties. The development of nanoscale photonic structures has been widely implemented in the last years [1, 2] thanks to the efforts and achievements obtained in nanofabrication processes such as Electron Beam (E-Beam) Lithography, Focus Ion Beam (FIB) or Dip-Pen nanolithography and replica molding. Because of its ease of application to a wide variety of materials, replica molding has been pursued as a general approach to repeatable production of nanostructured surfaces starting from a single, high-precision master. Optofluidics, emerged in 2003 thanks to the marriage between optics, nanophotonics and fluidics [3], refers to a class of adaptive optical circuits that integrate optical and fluidic devices. This integration represents a new approach which enables flexible fine-tuning and even dynamic reconfiguration of optical circuits [4]. Polydimethylsiloxane (PDMS) is often the material of choice for optofluidics due to its high optical quality, cast-molding capabilities, low

*Address correspondence to Luciano De Sio, Beam Engineering for Advanced Measurements Company, Winter Park, Florida 32789, USA. E-mail: luciano@beamco.com

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surface energy and in addition it is inexpensive and flexible [5]. PDMS is, however, a non-conducting polymer and to cross this problem several methods for integration of electrodes with microfluidic circuits have been developed, such as using highly doped silicon [6], single and multi-step optical lithography [7] or sputtering an Indium Tin Oxide (ITO) layer [8]. From a different point of view, despite the outstanding breakthrough enabled by utilizing nanotechnology techniques, the fabrication of a periodic structure with a periodicity equivalent to the visible wavelength is generally a high-cost process. Therefore, a self-assembled nanohelical structure such as Cholesteric Liquid Crystals (CLCs) would be advantageous for nanostructure fabrication. In addition, it is very well known that Liquid Crystals (LCs) are smart anisotropic materials having self-organizing properties, fluidity and can fulfil conditions imposed from outside, being responsive to a wide variety of external perturbations (AC, DC and optical fields) [9, 10]. Furthermore, the helical pitch of a CLC is easily controlled by external fields, temperature and mechanical stress [11]. Due to such large tunabilities, CLCs have been regarded as a potential candidate for the realization of tunable photonic crystals.

Liquid Crystals Optofluidics (LCO) has gained large attention in the last two years thanks to the possibility to realize a new generation of "active optofluidic" devices. In this framework, in a first attempt, we have combined azo-dye doped LC and 1D PDMS microstructures realized via replica molding [12]. The performances of the realized hybrid all-optical diffraction grating have been enhanced, in a second attempt, by functionalizing the PDMS surface with an amorphous SiO_x layer, thus lowering the optical response time by approximately one order of magnitude [13]. Pressure enables the LCs microflow, which has been recently employed for realizing an optofluidic modulator with enhanced optical properties and response time [14].

In this paper, we present a new method based on an ion-implantation process to pattern electrodes on a PDMS substrate; therefore, we have combined a conductive micropatterned and a uniform flexible substrate with the selective optical reflection of short pitch CLCs for realizing an electro-controllable and a pressure sensitive photonic crystal.

Materials and Methods

We used the E-BEAM lithography (Vistec EBPG5000, 100 kV acceleration voltage, at a dose of 5 μCb/cm^2) for direct resist patterning a microperiodic structure on a commercial available photoresist (SU8), spin coated on a silicon wafer. After trimethylchlorosilane (Sigma Aldrich) treatment of the master mold for 5 min, the PDMS (Sylgard 184, Dow Corning) is poured onto the mold with a 10 : 1 base to curing agent ratio. The curing process is performed in an oven at 70 °C for 1 h and subsequently the silicone is released from the mold. The grating period was 1.55 μm and its thickness approximately 1.5 μm.

Figure 1a is a Scanning Electron Microscopy (SEM) view of the implanted gold layer on the PDMS sample at the edge between the grating and the uniform area. It is worth noting that electrodes are implanted onto the sidewall and top wall of the grating area and are also very well connected across the borders into the PDMS microchannels, as confirmed also in the high magnification SEM picture reported in Figure 1b; here, due to the high energy of the electron beam, the PDMS channels collaps. We also measured the electrical resistivity of the conductive substrate by following a circular geometry (diameter 1 cm) around the grating area and measuring the resistance between the border of the circumference and the circle center. The polar diagram reported in Figure 1c confirms an almost uniform and symmetric resistance with an average value of about 50 Ω. The main advantage of the implantation

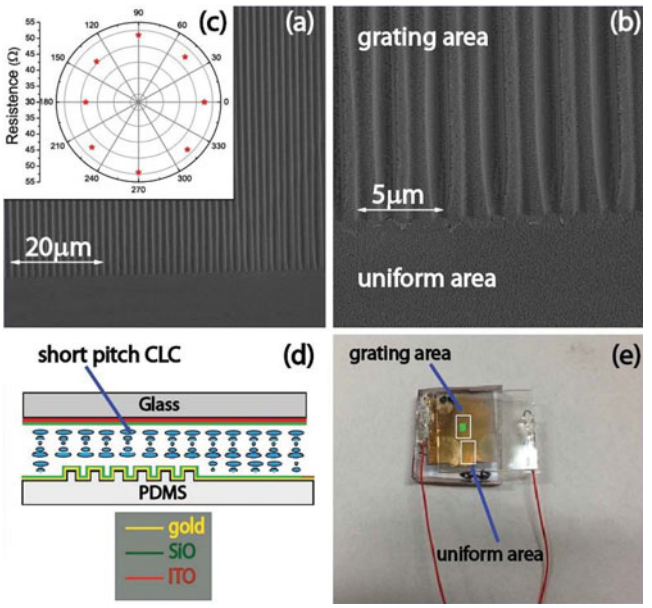

Figure 1. SEM view of the conductive PDMS microstructure (**a**) and its high magnification (**b**) Polar diagram of the resistance (**c**) Micrograph of the CLC configuration (**d**) in the aligning, electro-conductive, PDMS cell (**e**).

process with respect to our previous methods [8] is the excellent adhesion of the gold electrodes to the PDMS, since they are implanted a few nanometers below the surface. This level of adhesion was verified by using scotch tape on the surface of a PDMS surface with both sputtered and implanted gold. The scotch tape readily removed the sputtered gold from the PDMS surface while no noticeable change occured to the implanted gold. On the contrary, to obtain an excellent adhesion between the ITO layer and the PDMS substrate hard-backing was necessary to embed the ITO particles within the PDMS matrix. This step effectively increases the PDMS Young Modulus, introducing drawbacks in flexible devices applications. In a second step, we have functionalized the PDMS conductive surface by evaporating a thin layer of approximately 30 nm of SiOx according to the method previously reported for inducing a planar alignment of NLC on flexible substrates [13]. Therefore, the BL095 CLC by Merck (helix pitch $\approx$ 350 nm) was "sandwiched" between the PDMS microstructure (treated with gold and SiOx layers) and a modified ITO covered glass treated with a SiOx layer as shown in Figure 1d. The two surfaces were brought into contact via 4μm glass microspheres while the CLC was introduced by capillary flow at room temperature. Figure 1e is a picture of the electro-conductive PDMS sample; we have identified two zones marked with "grating area" and "uniform area". In the next sections, we will report experiments devoted to exploit diffraction and selective reflection of light in both zones respectively.

Electro-Switchable CLC Based Diffraction Gratings

Firstly, we analyzed the CLC alignment by means of a Polarized Optical Microscope (POM) technique after infiltrating the sample reported in Figure 1e.

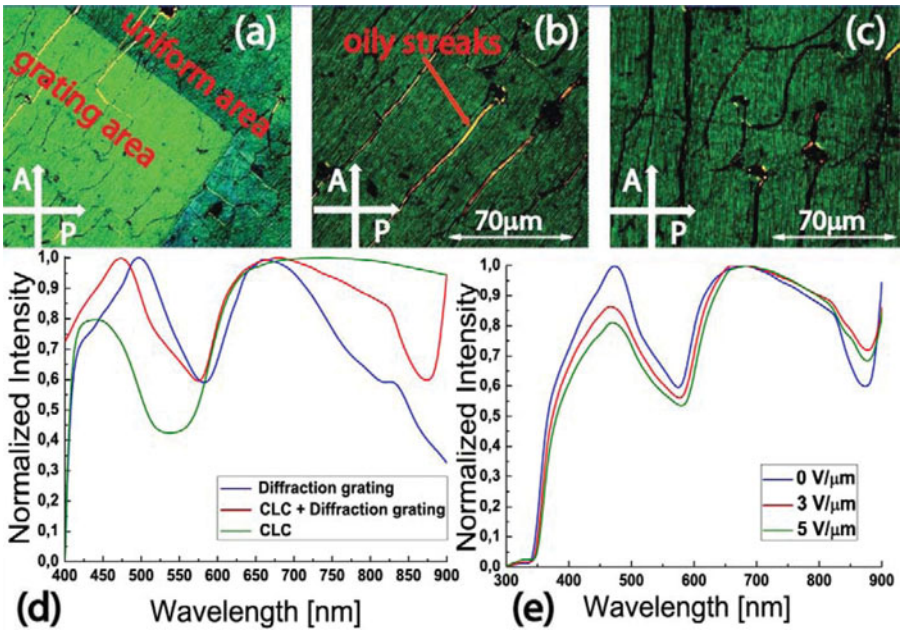

Figure 2. POM view of the sample infiltrated with CLC at the edge of the grating area (**a**). High magnification POM picture of the grating strips oriented at 45° (**b**) and 0° (**c**) with respect to the polarizers. Spectral characterization of the grating area (**d**) and its spectral response under the influence of an external electric field (**e**).

In the case when the CLC is confined between two substrates with planar anchoring, the director **n** is oriented parallel to the substrates and the helical axis is normal to the substrates (Fig 1d). Figure 2a is a POM view of the sample at the edge of the grating area where the presence of structural defects is clearly present. This kind of declinations are called oily streaks; in fact, in a flat cell with CLC layers parallel to the bounding plate, oily streaks appears as a long band that separates the ideal domains of flat layers. The inner structure is quite complicated and depends on many parameters such as elastic constants, surface anchoring and cell thickness. In any case, they are a marker of a lamellar phase and clearly confirm the Grandjean texture (CLC helices oriented perpendicular to the PDMS surface) of the CLC configuration[15]. To go deeper in details, we have acquired the high magnification picture of the grating area (Figure 2b) while rotating the sample between crossed polarizers (Figure 2c). By doing so, we did not observe any macroscopic variation of the optical contrast and this is a clear confirmation that the CLC is aligned in Grandjean configuration. In addition, the presence of the oily streaks is very well visible (highlighted in Figure 2b) and they exhibit a quite remarkable variation in the optical contrast (dark line, Figure 2c). It is very well known that CLCs aligned in Grandjean configuration exhibit a selective reflection band. Within the band, the circularly polarized incident light with the same handedness as the CLC is reflected while the opposite handedness is transmitted. The relationship between the Bragg wavelength (λ_b), bandwidth ($\Delta\lambda$) and pitch (P) of a CLC reflection band are shown in the simple relations of Eq. 1–3:

$$\lambda_b = \bar{n} P \tag{1}$$

$$\Delta\lambda = P \Delta n \tag{2}$$

$$P = \frac{1}{HTP\,[C]} \tag{3}$$

where $\bar{n}$ is the average refractive index of the mixture, Δn is the birefringence, HTP is the helical twisting power of the chiral dopant and [C] its concentration. To confirm the CLC alignment in Grandjean configuration, we have investigated its spectral response by probing the sample with unpolarized white light (wavelengths in the range 300–900 nm) at normal incidence; the obtained results are reported in Fig. 2d. The red curve is the spectral response of the grating area before infiltrating it with CLC; the transmitted light exhibits, therefore, a band-gap (centered at $\lambda = 595$ nm) due to the diffraction operated by the PDMS grating in this spectral range in accordance with Kogelnik's theory [16]. We have also analyzed the spectral response of the CLC by using a functionalized (planar alignment) glass cell (thickness$\approx 4\mu$m) and the result is reported in Figure 2d (green curve). According to equation (1), the CLC reflection band is centered at $\lambda_b \approx 540$ nm (whit $\bar{n} = \frac{n_e+n_o}{2}$**;** where $n_e = 1.63$ and $n_o = 1.50$ are the extraordinary and ordinary refractive index of the CLC respectively). This rough estimation is also confirmed in the spectral analysis reported in Figure 2d (green curve). To verify the CLC alignment on the PDMS grating and its influences on the diffraction properties of the sample, we performed a spectral analysis of the grating area of Figure 2b. It is worth noting (Figure 2d, blue curve) that the diffraction peak is blue-shifted, with the presence of a "shoulder" due to the overlap of the diffraction band with the reflection band. Despite the mixed character (diffraction / reflection) of the band, it seems that due to the presence of the grating, the CLC helices exhibit an angular distribution of the molecular director around the normal to the PDMS substrate. This is the reason why we did not observe a sharp reflection band like the one reported in the green curve of Figure 2d. In addition, it is evident the presence of a new diffraction band centered at $\lambda\approx$900 nm; this can be explained by considering that according to the Kogelnik's theory [16] a variation of the refractive index of the grating induces the presence of new diffraction band, with a resulting difference in the spectral behavior of the diffraction grating. Finally, to verify the switchable properties of our structure, we monitored the spectral response of the grating area (Figure 2b) while applying an external electric field (square voltage, 1 KHz). We can observe (Figure 2e) that increasing amplitudes of the electric field (from 0 to 5 V/μm) induce a distortion of the CLC helices, with a resulting suppression and shift of both the reflection and the diffraction band, respectively. We note that this behavior is well reversible and repeatable.

Electro and Pressure Sensitive Bragg Reflectors

We exploited the capability of the uniform PDMS surface (like the one highlighted in Figure 1e) to induce CLC alignment [17]. For this reason, we used a sample cell with the same properties (in terms of geometry and surface functionalization) having a flat PDMS conductive surface. We have elongated the CLC (BL095, by Merck) pitch by adding a small amount of NLC (E7 by Merck, 2% in weight). This procedure corresponds to decrease the concentration of the chiral dopant already present in the CLC; therefore, according to equation (1), the CLC pitch is increased ($\approx$ 390 nm).

Figure 3a is the spectral response of the sample area reported in Figure 3c (CLC aligned in Grandjean configuration) for different values of the external electric field (square voltage, 1 KHz). The electric field induces a deformation of the helices geometry with a consequent blue shift due to the decreasing value of the refractive index (in our case, a decrease, roughly estimated from 1.56 to 1.5); at the same time, the reflection band is gradually suppressed.

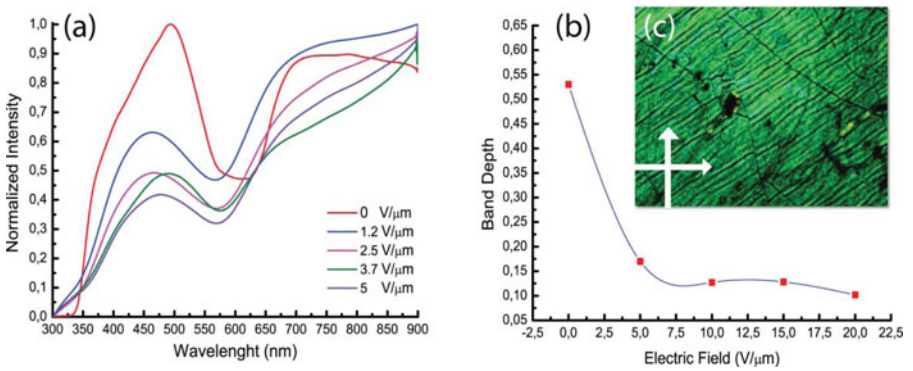

Figure 3. Spectral response (**a**) and band depth (**b**) behaviour of the sample for different values of the external electric field along with a POM view of the CLC alignment in the uniform area (**c**).

In fact, by plotting the band depth versus the electric field (Figure 3b) an "exponential like decay" behaviour is observed.

In order to exploit the soft PDMS substrate, we monitored the behaviour of the reflection band under the influence of an external pressure. To this end, we investigated the effect of conformal manual contact, frequently referred to as "touch band" and the results are reported in Figure 4a.

We induced a compression of the PDMS substrate by applying a symmetric pressure on the side of the cell by using both left and right index fingers according to the sketch reported in Figure 4b. By doing so, the CLC pitch is compressed and consequently, according to equation (1), the reflection band is blue-shifted of about 43nm. This is the reason why, in this particular experiment, we decided to increase the CLC pitch, since long pitch CLC enables the possibility to increase the shift of the band (ultra short pitch CLC is almost incompressible). We have roughly evaluated the fingers pressure range by measuring the weight force of our fingers (located at the same distance of the length of the cell) by means

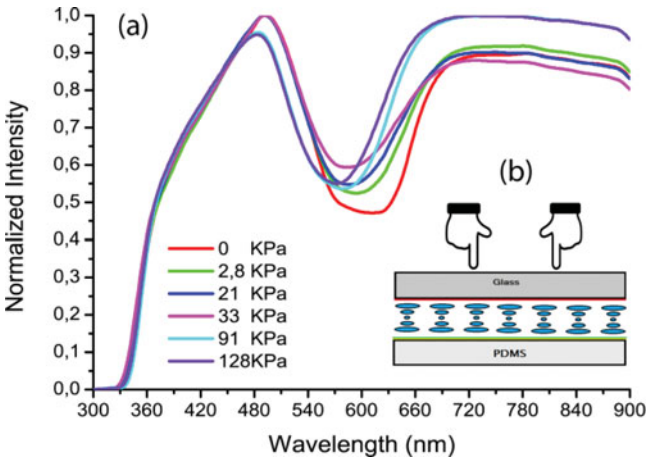

Figure 4. Spectral response of the sample versus the external fingers pressure (**a**). Sketch of the sample under the influence of the external pressure induced with the touch of fingers (**b**).

of a digital balance (sensitivity 1g). By doing so, we have established, in a roughly way, the pressure range applied on the sample, which is 128KPa.

Conclusions

We reported the realization of a new generation of optofluidic devices based on flexible microstructures combined with the extraordinary properties of reconfigurable soft-materials. In particular, we have combined e-beam lithography, replica molding and ion implantation process for realizing high quality and conductive flexible photonic structures. By means of a surface functionalization strategy, we have aligned the CLC in Grandjean configuration and exploited the selective Bragg reflection combined with the diffraction properties of a periodic structure. We have characterized the spectral features of the samples by using electrical field and pressure variations and exploiting a quite new concept named "touch band". These efforts represent a clear direction in building up a bridge between two branches of science: "Optofluidics" and "Liquid Crystals".

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