

# Silicon oxide deposition for enhanced optical switching in polydimethylsiloxane-liquid crystal hybrids

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**Abstract:** We report an optical switch based on a diffraction grating by combining PDMS microstructures with a photo-responsive Nematic Liquid Crystal (NLC). The grating was realized via replica molding and was subsequently coated with a thin SiO layer. SiO induced a full planar alignment of the liquid crystal. The induced parallel alignment of the LC reduces the response time of the structure by approximately an order of magnitude compared to the same structures without SiO. We explored the effect of the pump intensity on the transmission properties and time response of the switch and identified a strong dependence on the probe polarization, due to the full planar alignment in this structure. The aforementioned inclusion of the SiO layer enables enhanced performance of optical devices based on the fusion of nematogens with soft and flexible substrates.

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## 1. Introduction

Tunable photonic structures have attracted substantial attention in recent years for application ranging from information processing, and bio-analytical methods. In such periodic structures tuning may be achieved by using materials sensitive to external perturbations. Recently, we reported such an optical device by combining Nematic Liquid Crystals (NLCs) with elastomeric microstructures based on polydimethylsiloxane (PDMS) and demonstrated an optofluidic modulator capable of operating approximately more than one order of magnitude faster than conventional equivalent electro-optic devices and an optically controlled grating [1,2]. PDMS was employed due to its low-cost, high optical quality and compatibility with soft-lithography; these characteristics have recently positioned PDMS as an important material in microfluidics and optofluidics [3,4]. LCs and composite materials are of great interest in photonics. LC reconfiguration can be driven by several external stimuli, such as electric or magnetic fields, temperature and light [5,6]. For example, azobenzene derivatives are commonly to manipulate the anisotropy of the surrounding LCs by optically altering their stereochemistry. Recent efforts have focused on combining the photosensitivity of azo-dye doped Liquid Crystals (LCs) and azobenzene LCs (azo-LCs) with the diffractive properties of high quality periodic structures [7,8]. To this end, multiple material types and fabrication methods have been explored, primarily aiming at low cost and high repeatability [9,10]. Importantly, azobenzene and derivatives can undergo reversible trans-cis isomerization if irradiated at suitable wavelengths. Light diffraction is strongly affected by the optically induced anisotropy of the LC surrounding the dye resulting in the optically switched grating [11]. Unfortunately, for the majority of these dyes, UV light is needed to trigger the photoswitching, which degrades the physical properties of the LCs [12]. To avoid this problem, we use an azo dye doped LCs whose trans-cis isomerization process is induced with visible light. However, the effect of the photoisomerization on the host LC thus be expected to be stronger in presence of azo-LCs [13]. In our earlier work [2] on optically controlled switching in PDMS-nematogen media, we employed a NLCs doped with a low concentration Methyl Red (MR). The azo-dye MR appears to be a good candidate, since its absorption band of trans isomer is typically in the blue-green range and for low concentration its solubility in NLCs is high enabling the control of the optical anisotropy of standard NLCs. In the same work, we showed that without any additional surface chemistry the NLCs is spontaneously homeotropically aligned between the PDMS grating and the unmodified cover glass. By functionalizing the cover glass with a thin "polyimide" layer with a preferred planar direction, induced via rubbing, a hybrid orientation of the NLC was achieved. An all-optical controlled diffraction gratings was demonstrated in this geometry but in order to improve the performance of the device, a full-planar alignment of the NLC is preferable. To further enhance the performance of the soft PDMS elastomer in liquid crystal related applications, we present here a surface functionalization strategy capable of decreasing the optical response by approximately an order of magnitude. The introduction of amorphous SiO<sub>x</sub> layers deposited

on indium-tin-oxide (ITO)-coated glass substrates have been incorporated into liquid crystal displays, plasma display panels, thermal control windows, solar cells, etc [14]. In fact, glass coated with silicon oxide has been largely used to improve LC alignment.

## 2. Sample preparation

Here, we demonstrate the possibility to employ the SiO deposition in order to induce the full-planar alignment of LC on PDMS. To obtain a good planar alignment on a non-rigid substrate (PDMS surface), we utilized a Physical Vapour Deposition (PVD) technique which consists in a vacuum deposition method that deposits thin films by condensation of a vaporized form of the material onto various surfaces. In particular, we used an evaporative deposition method (evaporator equipment is an assembling of a rotative and turbomolecular pumps provided by Edwards; while the electronic controller is given by frequency counter, quartz crystal thin film provided by Balzers) in which the material to be deposited is heated to a high vapour pressure by electrically resistive heating at low pressure. We used SiO at a pressure of  $1.4 \cdot 10^{-6}$  mbar, at a current of about 225 A for a deposition time of 2 minutes. In this way we obtained a SiO film on PDMS microstructure with a thickness of about 30 nm. The NLC was the E7 (Merck) doped with MR at a 2% ratio in weigh. This suitable ratio has been chosen by taking into account the solubility of MR in NLC and the light sensitivity of the mixture in the visible range. The PDMS grating was fabricated by direct electron beam lithography on SU8 (Vistec EBPG5000, 100 kV acceleration voltage, at a dose of  $5 \mu\text{Cb}/\text{cm}^2$ ) and subsequent pattern transfer to PDMS via conventional cast molding. The grating period was  $2 \mu\text{m}$  and its thickness approximately  $1.5 \mu\text{m}$ .

## 3. Experimental results

In Fig. 1 we report the transmission spectrum of the mixture which exhibits a high absorption around 500 nm range while in the inset we show a polarized optical microscope view of the mixture in planar alignment in a glass cell treated with a thin “polyimide” layer, where a preferred planar direction was induced via rubbing.

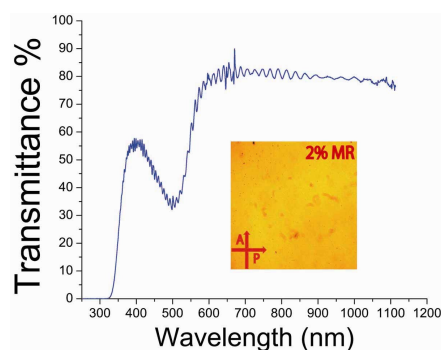


Fig. 1. Polarized transmission spectrum (polarization vector along the long axes of the NLC) of the mixture realized with an optical spectrometer. Inset: photo of the mixture taken with a 20X objective.

As is shown in the inset of Fig. 1, despite the low concentration of MR (2%) dissolved in NLC some agglomerates are still present due to the low solubility of the MR in liquid-crystalline materials. In any case, in order to minimize the presence of MR agglomerate, we have selected by means of optical microscope a large area of the structure where the presence of MR clusters was negligible. Based on polarization transmission spectra the rod-shaped MR is preferentially aligned in the same direction as the NLC molecular director. In fact, the anisotropic absorption coefficient of MR exhibits, in the case of NLC full in-plane aligned, an extinction ratio of about 0.3 for light polarized along the long axes of the NLC. On the other side, its value is reduced up to 0.15 for light polarized along the short axes of the NLC. At the same time, we have investigated the absorption coefficient of MR for a sample with hybrid

alignment; values are 0.26 and 0.19 for light polarized along the long and short axes of the NLC respectively. This result is a proof that in both experimental conditions (NLC full in plane and hybrid alignment) the absorption coefficients are comparable and the MR molecules are preferentially aligned in the same direction of the NLC molecules. On the other hand, this low concentration enables light responsivity of the dye-doped NLC with a low pump power density (20-30 mW/cm<sup>2</sup>). The light sensitive NLC was “sandwiched” between the PDMS microstructure treated with the SiO layer and a modified glass substrate treated with a “rubbed” polyimide layer as is shown in Fig. 2a.

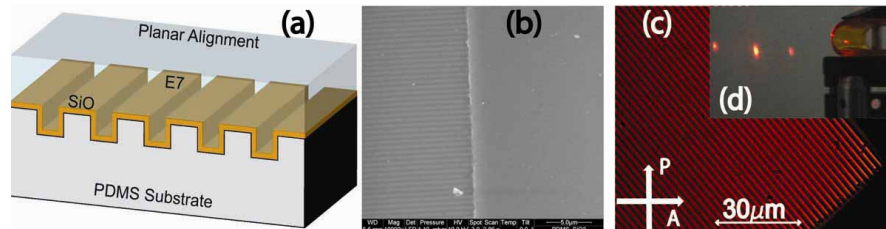


Fig. 2. View of the grating sample (a) and corresponding SEM image (b). In (c) is reported an optical microscope view of the sample along with the far field diffraction pattern obtained by probing with a He-Ne laser the flexible grating (d).

The two surfaces were brought into contact via 1.5 μm glass microspheres while the sensitive NLC was introduced by capillary flow in the isotropic phase (65 °C). The sample was slowly (0.5 deg/min) brought below the isotropic- nematic transition point (typically, down to room temperature) in order to drive the NLC orientation. The scanning electron microscopy (SEM) picture of the grating structure after the SiO deposition is shown in Fig. 2b while the Polarized Optical Microscope (POM) view of the sample infiltrated with light-sensitive NLC is shown in Fig. 2c. In order to characterize the NLC alignment, we performed optical experiments by using the probe-pump setup already described in [15]. We monitored in Fig. 3 the first-order diffraction efficiency behavior versus the polarization angle of the impinging probe radiation (He-Ne laser, λ = 633 nm) for different values of the external pump power (Diode laser, λ = 532 nm). Probe light polarized orthogonal to the grating stripes (p-polarization) will experience a high index contrast ( $n_e - n_{pdms} \sim 0.3$ ) while light polarized along the grating stripes will experiences a low index contrast ( $n_o - n_{pdms} \sim 0.1$ ). Where, we have indicated with  $n_e$ ,  $n_o$ , the extraordinary and ordinary refraction index of the NLC respectively while  $n_{pdms}$  is the refractive index of the PDMS material.

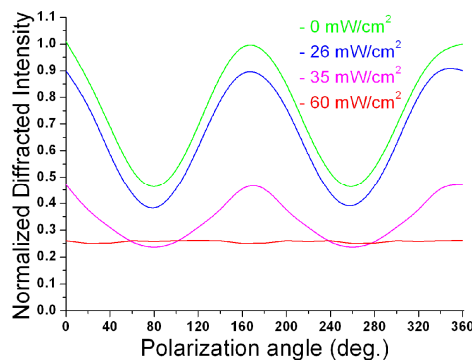


Fig. 3. Normalized diffracted Intensity versus the polarization angle of the impinging probe beam for different values of the external pump power.

The diffraction efficiency of a periodic structure is strongly related to the index contrast [16]. If we define the normalized optical selectivity as the difference between the higher and lower value of the diffracted intensity, Fig. 3 indicates that the diffractive structure exhibits a high optical selectivity (green curve) of approximately 0.5. Therefore, the optical selectivity

can be controlled by irradiating the probed grating area with the external pump beam. In fact, due to photosensitivity of the MR, the NLC order can be destroyed by turning on the external pump power and the normalized optical selectivity can be controlled and reduced to zero (red curve). This behavior is due to the trans-cis photoisomerization process of MR which destroys the NLC order in the illuminated area and therefore the material becomes locally isotropic [17]. We have investigated the dynamics of the structure by monitoring the diffraction efficiency for different values of the pump power density from  $6 \text{ mW/cm}^2$  to  $61 \text{ mW/cm}^2$  while the probe power density ( $P_{\text{probe}} = 0.57 \text{ W/cm}^2$ ) is kept constant. This value has been founded experimentally in order to maximize the switching off time of the sample. In fact, the probe beam can speed up the cis-trans back relaxation time as has been demonstrated in ref [13]. Results are reported in Fig. 4.

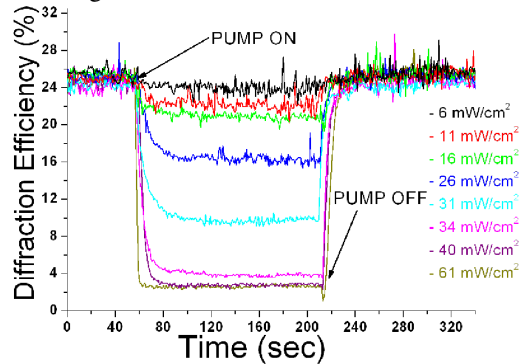


Fig. 4. Diffraction efficiency versus the time. Curves have been acquired for different values of the pump radiation.

Figure 4 clearly shows the strong correlation between the variation of the diffraction efficiency and the external pump power value. At the same time, the response time is a function of the impinging pump power. This behavior can be explained by assuming the rate of concentration of photoisomerized molecules is proportional to the incident intensity.

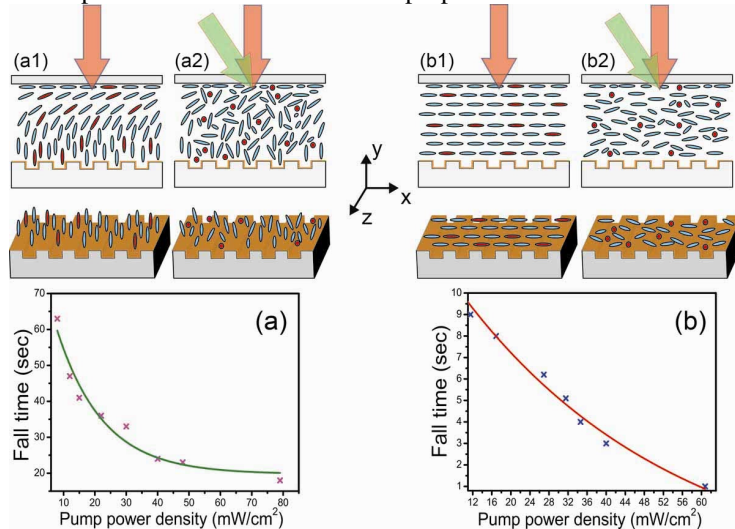


Fig. 5. Comparison of the fall times of the structure without (a) and with SiO treatment (b) versus the pump power density. (a1, b1) and (a2, b2) are the hybrid and planar conditions before and after the pump irradiation respectively. The probe and pump beam are both polarized along the x direction.

To confirm the performance of the structure induced by the SiO surface treatment, we report in Fig. 5 a comparison of the fall time of the above described structure, with our

previous results obtained without using any PDMS surface functionalization strategy. The response time of the samples was measured by varying the on-value of the pump power while the probe one is kept constant. By increasing the pump power density, it is possible to reduce the fall time, which can be varied from 65 to 20 seconds in the case of the structure without SiO treatment (Fig. 5a), while they can be significantly reduced until down to 1 second in the case of the SiO coated PDMS grating (Fig. 5b). We attribute the strong difference in the fall time is due to the NLC alignment modification from hybrid to planar configuration (Fig. 5a1-b1). In the case of hybrid configuration the trans-cis isomerization process induces a bulk reorientation (“splay/bend like” in the xyz plane) of the molecular layers which are homeotropic to the PDMS surface (Fig. 5a2). In the case of planar configuration the trans-cis process induces a full in - plane reorientation (Fig. 5b2) of the NLC molecular layers which are planar to the PDMS surface (“twist like” in the xz plane) which is a low energy transition with respect to the bulk one. It is well known [5] that due to the direct connection to the different elastic constants, the “twist like” elastic deformations are much faster than the “splay/bend like” ones. This analogy manifests itself in the observed experimental difference in the turn-off times. In both cases, the data are well fitted by the negative exponential curve reported in [15] and at the same time the range variation and the dynamics of the turn-on time follow the same behaviour already described for the fall time. However, by performing a UV-Visible spectral scan, we observed a non-reversible and fast decomposition of both samples after several cycles of pump irradiation. Indeed, as has been already shown [18,19], non-mesogenic azo dyes (e.g. MR) act as impurities, reducing the order parameter of the host LC material; furthermore, they have the tendency to separate from the LC, sedimenting on the boundaries and changing the boundary conditions. For this reason they are not suitable for the fabrication of repeatable all-optical devices and the employment of high performance mesogenic azo-LC is then required [13].

#### 4. Conclusions

In conclusion, we report the alignment of a NLC on a flexible PDMS substrate in planar alignment. We accomplished this by coating the PDMS diffraction grating with a thin SiO layer. This surface treatment combined with a modified cover glass enables the full in plane alignment of the NLC. All-optical experiments were carried out to characterize and monitor the versatility of the process and showed that the SiO coated gratings exhibit an enhanced time-domain performance compared with the bare PDMS surfaces.

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