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Sub-millisecond nematic liquid crystal switches using patterned command layer

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Switching speeds of nematic liquid crystal (LC) cells in the sub-millisecond range are observed for 3-D patterned self assembled monolayers (SAMs) on indium-tin-oxide (ITO) substrates. To achieve such fast LC response and relaxation times, thermal treatments of the patterned SAM-on-ITO are required, increasing the relative anchoring energy experienced by the interacting LC molecules.

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I. INTRODUCTION

One of the outstanding characteristics of liquid crystal (LC) devices is the possibility to control their molecular alignment over long distances (μm), thanks to their long-range orientational order combined with their high sensitivity to external stimuli, like magnetic and electric fields.

These unique physical properties make them very attractive materials for many applications, such as LC displays (LCDs),1 spatial light modulators,2 sensors,3,4 and for the manipulation of guest materials serving as a tunable anisotropic host.5–7 LCDs offer a wide range of advantages such as high resolution, high sharpness and brightness, zero geometric distortion, light weight and low power consumption. A major drawback of LCDs, however, is their slow response times, causing severe image degradation for moving or rapidly changing images.

Several technologies are currently under development to realize faster switching LC devices. These range from changing the LC cell geometry and electrodes design,2–11 to changing the LC structure from cholesteric to blue phase (BP).12–16 Jo et al.8 combined two different LC cell architectures, the vertical alignment (VA) in the initial state and the four-domain twisted nematic (FDTN) with an external field stacking the VA layer onto the planar alignment layer, resulting in a rise time of 13 ms and a driving voltage of 6 V. Tae-Hoon Yoon et al.9 introduced a three-terminal electrode structure to simultaneously apply an in-plane and a vertical electric field, to show both bright state and grey levels, with the slowest grey-to-grey response of 9.6 ms and from grey to zero in less than 1 ms. Hun Ki Shin and collaborators30 proposed a polarization switching device using an optically compensated pi cell for polarization-glass-type three-dimensional display with a total dynamic response time of 2.5 ms. Won-Kyu Lee and collaborators11 developed a new LC alignment layer combining single wall carbon nanotubes (SWNT) with a conjugate block copolymer and conventional rubbing. Yielding a high response time (3.8 ms), low operation voltages (1.3 V), and high thermal stability.

Moving to a different approach, where different types of LCs are used, Cholesteric LCs can be good candidates for several devices because of their bistability and high reflectance but their major drawback is the high driving voltage required to operate the cell, reaching tens of volts.12,13

Recently a different class of LCs has emerged as a promising candidate for photonic and display applications, namely polymer-stabilized BP LC.14–15 Jin Yan and Shin-Tson Wu16 demonstrated a tunable phase grating using such LC, with high diffraction efficiency and submilliseconds response time but, as in the previous case, a driving voltage in the order of hundreds of volts. Choi et al.17 recently investigated the electro-optic response of BPII blue phase LC with different chiral pitch, showing again really fast responses, less than 1 ms, but still high driving voltages.

All these approaches show clear disadvantages. In fact, to obtain sub-millisecond (ms) performances, high operating voltages (up to 100 V) are used,12,13,16,17 while in the case of low operating voltages (below 50 V) typical switching times are longer than 10 ms or complex and elaborated architectures and materials need to be used.9,10,18

Increasing attention has been devoted to micropatterned alignment surfaces, thanks to their flexibility in controlling the main LC alignment properties, such as pretilt angle and anchoring energy, compared to unidirectional alignment methods.19–30 Yokoyama and coworkers19 demonstrated already more than 10 years ago that by nanorubbing a polyimide layer with an atomic force microscope, it was possible to locally manipulate the LC alignment from planar to orthogonal between neighboring domains on the same surface. More recently, nanoimprinting and photoalignment techniques have been employed to build more complex micropatterned surfaces to form bistable LC devices.26,30

Patterned self-assembled monolayers (SAMs) on glass or indium-tin-oxide (ITO) substrates appear to be a promising solution to design surfaces capable to modulate the polar orientation of supported nematic LCs at the micrometer scale, passing from homeotropic to planar alignment depending on the geometry and periodicity imposed by the pattern.20,31–35

Here, we propose sub-ms and low voltage nematic LC switching based on very simple 3-D patterned SAMs on ITO substrates. The structured surfaces were obtained by a local mask-assisted UV-light removal of a self-assembled organosilane monolayer.20,33 The patterned structure was baked at
120 °C for 1 h to optimize the surface anchoring energy, which plays an important role in the final device performance. Using a conventional single step photolithographic process to transfer a geometric pattern onto a LC aligning layer, without further chemical treatments, makes this approach particularly suitable for large scale industrial applications.

ITO plates, covered by a uniform SAM of octadecyltri-methoxysilane (OTMS), are known to generate a homeotropic alignment of LC molecules. These SAMs were subjected to UV photodecomposition using an excimer laser and a photo-mask to pattern the surface. The resulting bare ITO surface gives rise to planar alignment with a free-azimuthal direction, following exactly the geometrical pattern imposed by the mask. This method yields a bi-functionalized pattern surface able to align the LC molecules.

The thermal annealing step of the organosilane SAMs was demonstrated to induce the immobilization of adsorbed siloxane molecules and their packing, either by the attachment to the underlying substrate and/or surrounding silane molecules or by the removal of adsorbed water. This improvement of the SAM properties suggests a possible different LC-SAM interaction, and a different anchoring energy. Therefore, thermal treatments were performed at 120 °C for 1 h on both top and bottom SAM-on-ITO plates, before the UV-patterning and the cell assembly.

II. EXPERIMENTAL

The ITO substrates were purchased from PGO Germany (Product code: CEC1008). The cut ITO slides 11 × 11 mm² were ultrasonically cleaned with detergent (ALCONOX) for 30 min and rinsed with copious amounts of tap water. They were immersed and stored (24 h) in a base bath cleaning solution (KOH and ethanol). Then they were ultrasonically cleaned in fresh MilliQ-water (18.1 MΩ · cm), followed by acetone (99.8%, Merck) and 2-propanol (Fluka 99.9%). At last, they were blown dry with N₂ and treated with a UV/ozone cleaner (Novascan Technologies, Inc.).

The fabrication of a patterned ITO surface was performed starting from the preparation of 0.5 mM OTMS (≥90%, Sigma Aldrich) solution in toluene (≥99.97%, Fisher Scientific). After the OTMS solution was prepared, the cleaned ITO substrates were immediately submerged in the solution for 2 h at 60 °C. The substrates were then ultrasonically rinsed in fresh toluene to remove any non-covalently bonded molecules. Finally, they were blown dry with N₂. In the case of the baked samples, the SAM-on-ITO plates were baked at 120 °C for 1 h.

UV-lithography was performed through a contact-mask characterized by different square size patterns. In detail, we used two squared patterns: 4 × 4 μm² square width (SW) and 10 μm periodicity (P) and 2 × 2 μm² SW and 6 μm P. An argon fluoride excimer laser (193 nm) was used as UV-source and a total dose of ~9 J cm⁻² was applied to photochemically remove the OTMS SAM. To remove the photo-cleaved products, the patterned substrates were soaked in ethanol for 30 min and finally blow dried with N₂.

LC cells were assembled using one patterned and one not patterned SAM-on-ITO surface glued with a UV-curable glue (NOA65, Norland). The cell gap of 4.0 μm was guaranteed by using embedded particles (Licristar, Merck) into the glue. The cells were then filled with LC material BL087 (Merck) by capillary force at 100 °C (T\textsubscript{IN-BL087} ~ 89 °C). The filled cells were kept at 100 °C, in the isotropic phase, for a few minutes before they were cooled to room temperature. The cooled cells were finally sealed with epoxy glue (Epoxy Rapid, Bison). As reference, we prepared also a cell combining two ITO plates, one with a uniform SAM while the other was exposed to the excimer laser to remove the SAM without the photo-mask, in order to see if the laser ablation itself can affect the LC switching dynamics.

Optical microscopy images were obtained with an Olympus BX60 microscope, objective Olympus 40× (NA = 0.55) or oil immersion Nikon 100× (NA = 1.3), viewed in white-light transmission or filtered (Olympus IF 546) between crossed polarizer and analyzer. Contact angle (CA) measurements have been performed by using a drop shape analyser (DSA) 100 from Kruss with the sessile drop method. For studying the LC director configuration in dynamic condition, fast recording optical images were acquired by using a high resolution 14 bit CCD cooled camera system PCO-2000, connected with a 100× objective, in transmission configuration and illuminating the sample with polarized white light.

III. RESULTS AND DISCUSSION

When the electric field is switched on (5 V), LC molecules in the square domains are forced to rotate from a planar to a homeotropic alignment, as represented in the passage from Figures 1(c) to 1(d). In particular, it can be observed in the inset of Figure 1(d) that the cell appears completely black, indicating that the molecules in the square domains are switched and that the homeotropic walls (black matrix in Figures 1(a) and 1(b)) are not affected by the external field. Thanks to the presence of these homeotropic walls, each square can switch independently from the others, avoiding flow-induced dynamic cross-talk between neighboring switching LC domains.

It can be observed (see Figures 1(a) and 1(b)) that the LC molecules inside each planar domain do not assume a random azimuthal configuration, appearing bright when the boundary lines are at 0°/90° with respect to the polarizer (Figure 1(a)) and dark when the boundary lines are at 45° with respect to the polarizer (Figure 1(b)). This means that the central part of the LC molecules prefers to lie along the diagonal axes of the squares, while in the dark corners the director is aligned along the two orthogonal boundary lines. Moreover, the insets in Figures 1(a) and 1(b) underline the four stable alignment states that can be generated. Each configuration differs from the others not only by a simple in-plane rotation of 90° but also by an opposite surface tilt angle assumed by the LC molecules along one of the diagonal axes. This organization minimizes the elastic-distortion energy introduced by the homeotropic LC boundaries, as reported by Zhang et al.
In order to investigate the LC molecules interactions with the patterned SAM-on-ITO surface, deionized water CA measurements were performed (see Figure 2), using a DSA 100 from Kruss with the sessile drop method. These experiments were carried out by releasing a 3 µl water drop on different substrates: clean ITO surfaces, not irradiated OTMS SAM-on-ITO and irradiated SAM-on-ITO surfaces (without photo-mask), both for the baked and not baked case. For the irradiated samples, both exposed and not exposed zones were separately tested. As can be observed in Figure 2, the water CA on a not exposed SAM (full squares) is slightly higher than 100° for both baked (red squares) and not baked (black squares) cases.

In contrast, the irradiated-exposed SAM (empty squares) presents an abrupt shift towards more hydrophilic CA values (58°–59°) as indicated by the black arrow in Figure 2, in agreement with previous studies. This abrupt increase in wettability, and thus decrease of hydrophobic surface energy, is the result of SAM degradation, under UV-light exposure. This shift in water CA measurements between exposed and not exposed SAM can qualitatively explain the transition of LC anchoring from homeotropic to approximately planar.

Optical microscopy images of two samples, one thermally treated (Figure 3(a)) and the other one not (Figure 3(b)), show a change in color of the square planar domains, from orange to yellowish green. By consulting the Michel-Lévy color chart, it can be deduced that this color shift corresponds to a decrease in birefringence of about 10%. In fact we deduced a reduction from 0.2 in the not thermally treated case (Figure 3(a)), close to the nominal value reported in the nematic BL087 data sheet ($\Delta n_{BL087} = 0.23$), to 0.18 in Figure 3(b). This can be directly connected to an effective reorientation of the LC molecules towards higher polar angles, therefore a higher anchoring energy.

In order to test these performances, electro-optical switching curves were recorded by applying a square wave signal from 0 to 5 V, at 200 Hz, and measuring the transmission of a He-Ne laser ($\lambda = 632.8$ nm) at normal incidence. The cells were mounted between crossed polarizer and analyzer and positioned with the boundary lines, respectively, at 0°/90° to the polarizer. For reproducibility, the reported
facilitates the field-assisted transition from planar to vertical (fast $\tau_{\text{on}}$ and low $V_{50\%}$) but, surprisingly, not the reverse transition (long $\tau_{\text{off}}$). Apparently, the free LC molecules in the planar domains (green squares in Figure 1(a)) are subjected to a sort of pinning effect, presumably caused by the presence of the homeotropic walls during the relaxation transition.

The most clear and remarkable result is the decrease in switching times for the baked and patterned SAM cells (Figure 4, black and red symbols). Both $\tau_{\text{off}}$ and $\tau_{\text{on}}$ appear under 1.5 ms, while maintaining a $V_{50\%}$ at the extremely low value of 2 V. Furthermore, not only did $\tau_{\text{off}}$ decrease but also has become faster than $\tau_{\text{on}}$. The performances of not patterned cells (Figure 4, full symbols), on the other hand, do not seem to be affected by the thermal treatments, except for the $V_{50\%}$ which is reduced by 1 V in the case of baked SAM.

The fact that, in patterned LC cells, the annealed SAM results in a considerable improvement of the electro-optical performances suggests that the interaction between the LC molecules and the aligning layer is not only connected with the SAM wettability, measured with the contact angle, but also with the SAM molecular structure, as clearly appears in Figures 3(a) and 3(b). A thermal treatment, in fact, reorganizes the SAM density and attachment to the ITO surface, reordering the alkyl chains packing and removing potential absorbed water, allowing not only a reorientation of the nematogens towards much higher polar angles (see Fig. 3(b)) but also a much deeper penetration into the monolayer.38

These two effects, in turn, increase the LC molecules anchoring energy, i.e., the parameter that quantifies the alignment of the LC molecules, making any deviation from the initial aligning condition more difficult and affecting the switching times of the whole LC cell.

These observations can also be understood in a more quantitative way. The expression for the LCs cell relaxation time for a finite surface anchoring energy ($W$) is39

$$\tau_{\text{off}} \approx \frac{\gamma_1}{K} \left( \frac{d^2}{W} + \frac{4dK}{W} \right),$$

(1a)

where $\gamma_1$ is the LC viscosity, $K$ is the bend elastic constant (one constant approximation), and $d$ is the cell thickness. Under strong anchoring conditions, where $4K/W \ll d$, the equation suggest $\tau_{\text{off}} \sim d^2$, while in the weak anchoring condition case, where $4K/W \gg d$, the LC relaxation time is reduced to

$$\tau_{\text{off}} \approx \frac{4\gamma_1 d}{W \pi^2},$$

(1b)

which is directly proportional to the inverse of the anchoring energy. Expression (1b), together with the increase polar angle observed in Figure 3, can explain the enhancement of the electro-optical performances due to the thermal treatments. By increasing the LC anchoring energy $W$ by the baking process, and keeping $d$ and $\gamma_1$ fixed, within the condition $4K/W \gg d$, the relaxation time $\tau_{\text{off}}$ becomes shorter. At the same time, if we think that the LC molecules in the case of annealed SAM, arrange with a higher polar angle, when the electric field forces their homeotropic alignment, the rotation

values are an average of three different measurements, each related to a different LC cell.

Figure 4 gives the response time $\tau_{\text{on}}$ (the time required by the LC molecules to align along the field), the relaxation time $\tau_{\text{off}}$ (the time required by the LC molecules to restore to the initial position), and the voltage at 50% of transmission ($V_{50\%}$) for each type of LC cell.

For unannealed samples, the patterned cells (empty black squares) present a lower $V_{50\%}$ compared to the not-patterned ones (full black squares), meaning that LC molecules when in contact with the patterned SAM require less energy to align along the external field. In terms of switching times, $\tau_{\text{on}}$ presents quite promising values (2 ms) with no particular differences between the patterned or not-patterned SAM. The main difference is observable for the relaxation time $\tau_{\text{off}}$, reaching 4 ms on average with widely spread values in the case of the patterned LC cell, and 1.3 ms in the case of the not-patterned SAM LC cell, being even faster than $\tau_{\text{on}}$.

It appears that the presence of the homeotropic walls created by the patterned SAM (black areas in Figure 1(a))
they have to experience is shorter and so entire process results faster.

In current LC applications, driving voltages can reach 10 V or even higher values. By repeating the previous electro-optical measurements by applying an AC signal amplitude of 10 V (10 Hz), we observed sub-ms full dynamic LCs cell characteristics for baked and patterned SAM cells. We measured a $\tau_{\text{off}}$ of 0.65 ms, almost field-independent (0.62 ms at 5 V), and a clearly shorter $\tau_{\text{on}}$ from 1 ms (5 V) to 0.34 ms (10 V), directly related to the increase of the torque imposed by the increased external field.39

As previously mentioned, the LC molecules can be subjected to pinning effects at the transition from homeotropic to planar alignment domains (see Figure 5). At the edges between these two domains, in fact, the nematic director tries to find an equilibrium, in which the Frank elasticity enforces the inhomogeneity near the edge to relax into the uniform bulk orientation over a characteristic length of the order of the pattern size, as schematically represented in Figure 5. Therefore, the LC molecules organization near the pattern-edges deviates from that in the adjacent regions, being perturbed over a certain length not only in the z direction (perpendicular to the substrates, see Figure 5) but also in the x-y plane (parallel to the substrate, see Figure 5), depending on the strength of the alignment in these surrounding regions.20,24

To investigate the behaviour and the extension of these pinning effects, the electro-optical performance was recorded with a fast recording camera (see Figures 6(a) and 6(b)), and the switching times ($\tau_{\text{on}}$ and $\tau_{\text{off}}$) together with voltage required to reduce the transmission to 50% ($V_{50\%}$) were measured as a function of the pattern size (see Figure 6(c)).

Figures 6(a) and 6(b) show the transmission optical images of the switching of two different samples by applying a square wave signal (amplitude 0–5 V and frequency of 10 Hz) and illuminating with polarized white light. In the case of the $4 \times 4 \mu m^2$ square pattern, it appears that just the central part of each square is free to switch completely from planar to homeotropic (see Figure 6(a')), forming a diamond-like bright region in contrast to the thick and dark corners frozen by the boundary interactions. This situation is even more dramatic for the $2 \times 2 \mu m^2$ square pattern (see Figure 6(b')), where, at the turning-on of the voltage, there are no bright areas, meaning that the whole volume is partially pinned by the edge perturbation (see Figure 6(b')) and the LC can only slightly tilt (reduced image contrast) but not completely.

![Figure 5](image_url)

**FIG. 5.** Schematic view of the distribution of the LC molecules onto a SAM patterned with only one square. LC molecules are represented by prolate spheroids aligned planarly into the SAM UV exposed square blue area, and homeotropically in the surrounding orange frame. Such LC planar organization was deduced from optical microscopy images reported in Figures 1(a) and 1(b).

![Figure 6](image_url)

**FIG. 6.** (a) Transmission optical images of the switching of two different samples by applying a square wave signal (amplitude 0–5 V and frequency of 10 Hz) and illuminating with polarized white light. (a) and (a') correspond to the square $4 \times 4 \mu m^2$ pattern at 0 and 5 V and P-in at 45°; and (b) and (b') show the square $2 \times 2 \mu m^2$ pattern at 0 and 5 V and P-in at 135°. (c) The average response time $\tau_{\text{on}}$ (filled squares), relaxation time $\tau_{\text{off}}$ (empty squares), and voltage (red circles) at 50% of transmission ($V_{50\%}$), as a function of the pattern size $4 \times 4 \mu m^2, 2 \times 2 \mu m^2$ and $1 \times 1 \mu m^2$, respectively.
unchanged, maintaining a value below 2 ms. In contrast, the relaxation time increases from 3.5 to more than 7 ms, possibly caused by the increased LC edge-perturbation as the pattern size decreases. On the other hand, the operating voltage $V_{50\%}$ does not seem to be much affected by the pattern size, ranging from 1.5 V to 2.5 V.

The pinning effects explain the degradation of the electro-optical performances as the pattern size is decreased. This implies that the modulation of the LC director orientation has a spatial threshold, preventing the possibility to scale the pattern below 4–5 μm and fixing, as a consequence, the maximum display spatial resolution in such devices.

IV. CONCLUSIONS

In conclusion we demonstrated that 3-D patterning of organosilane SAMs on ITO surfaces is a promising and reliable technique to control the polar anchoring of nematic LCs, showing extremely competitive electro-optical performances (sub-ms switching at 10 V applied field) for current industrial applications. We observed that by patterning the SAM-on-ITO, LC cells present an almost halved voltage at 50% of transmission but a longer relaxation time compared to the case of LC cells without a pattern. We explained that by assuming the presence of pinning effects at the edges between homeotropic and planar domains.

In particular, the presence of such perturbed boundaries results in a spatial reduction of the active area, limiting the minimum size effectively usable for applications.

In addition, we observed that thermal treatments of the SAM-on-ITO lead to substantially faster LC response ($\tau_{on}$) and relaxation times ($\tau_{rel}$). We interpreted this result as a consequence of the increased LC anchoring energy, especially in the not UV-exposed zones, thanks to the improved SAM properties after the annealing (ordered alkyl chains packing and siloxane-ITO bonds reinforcement).

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