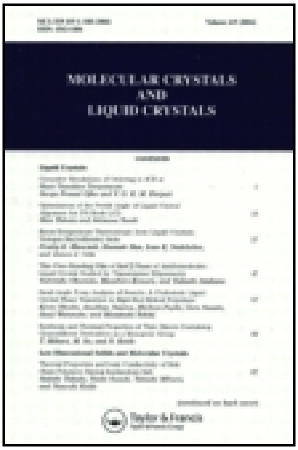

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The Multimode LC Alignment on the Substrates Obliquely Treated with a Plasma Flux

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The Multimode LC Alignment on the Substrates Obliquely Treated with a Plasma Flux

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We describe a variety of liquid crystal (LC) alignment modes on the aligning substrates obliquely treated with a flux of accelerated plasma from the anode layer thruster (ALT). The discharge area has a form of race track so that the generated flux contained two sheets of plasma corresponding to linear parts of the discharge. Within each "sheet" the intensity of flow (ion current density) is uniform in the direction parallel to the linear part of discharge. Across the "sheet", the intensity of flow has the Gaussian distribution. The alignment of LC with positive and negative dielectric anisotropy, $\Delta\varepsilon$, was tested on the substrates of organic (polymers) and inorganic (glass and DLC) origin treated in static and dynamic regime (unidirectional translation perpendicularly to plasma "sheet"). In the dynamic *regime of irradiation, with the substrate moving with respect to the plasma beam, for LC with $\Delta\varepsilon > 0$ we observed two aligning modes, with the easy axis confined to the plane of plasma incidence (mode 1) or perpendicular to this plane (mode 2). In the 1st aligning mode the LC pretilt angle is non-zero and can be varied with the incidence angle of plasma beam and the irradiation dose. With the increase of irradiation dose, the alignment transition from the 1st to the 2nd mode occurs. For LC with $\Delta\varepsilon < 0$ only the 1st alignment mode uniform over all substrate was observed. In the static regime of irradiation, characterized by smooth distribution of the particle's flow across the sheet, two modes are clearly observed simultaneously; 2nd mode alignment occurs in central, most intensive part of flow, while*

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the periphery part shows the 1st mode. The areas of the 1st and the 2nd mode are separated with the narrow transition area showing multidomain (two-fold degenerate) LC alignment. The easy axis in these domains is turned by about $\pm 45^{\circ}$ *with respect to the alignment direction in the 1st mode area. This sequence of the alignment transitions is observed in both LC with* $\Delta\varepsilon > 0$ *and* $\Delta\varepsilon < 0$*. We also describe a high-tilt alignment (*87°*–*90°*) in the 1st mode realized on the hydrophobic polymers at the extremely low doses of plasma irradiation. The origin of the observed alignment effects is discussed.*

Keywords: anode layer thruster; liquid crystal alignment; particle beam alignment; plasma

1. INTRODUCTION

The particle beam processing (PBP) is a general name of methods consisting in the oblique treatment of LC aligning substrates with a directed flux of particles (atoms, ions, electrons or mixtures thereof), which deposit on the substrate [1–3] or etch it [4,5]. As the result, the aligning surface becomes anisotropic and capable of LC alignment. Avoiding mechanical contact with the aligning substrate, PBP methods minimize surface damage and contamination. Simultaneously, they improve alignment uniformity and simplify pattering of LC alignment. Due to this PBP methods are very promising candidates to replace the traditional rubbing procedure for LC alignment in the next generation of LCD.

The PBP methods have a two-decade history, which was started with the works of Janning [1] on vapor deposition of SiO_x anisotropic layers and of Little *et al*. [4] on oblique treatment of the aligning films with the ion fluxes of high energy (1–3 keV). The renewed interest to PBP methods was sparked by the recent publication of the IBM group [6,7]. Their procedure is similar to the procedure of Little *et al*. [4], but ion energy is reduced to 50–300 eV to modify only the very top layer of the aligning film. These treatment conditions are achieved by the use of the ion source of Kaufman type. According to [6,7] the method provides excellent LC alignment on both organic and inorganic substrates.

As we showed earlier [8–11], the ion beams can be successfully replaced for the purpose of LC alignment with the beam of accelerated plasma. The first attempts in this direction were made with Sprokel *et al*. [12]. To treat or deposit aligning layers they used the "cold" r.f. plasma carried to the substrates with the directed gas stream. In contrast to this, we used the plasma beam that is extracted and accelerated electrostatically. The energy range of accelerated ions was chosen to be comparable with that used in IBM experiments.

All this conditions were realized by the use of an anode layer thruster (ALT) generating sheet-like fluxes of Ar plasma [13]. By carrying out irradiations in the static regime (the samples and source do not move) we observed two alignment modes: (1) one with the easy axis confined to the incident plane formed by the direction of the beam and the normal to the treated substrate; (2) the second mode with an easy axis that is perpendicular to the plane of incidence. In the 1st mode, LC pretilt angle θ is non-zero and can be controlled , while in the 2nd mode it is zero. The transition from the alignment type (1) towards the type (2) can be realized by increasing the irradiation dose. As we recently found, the 1st and the 2nd mode may be separated with the transient modes. In the present paper we describe a variety of the aligning modes in the static and dynamic regime of irradiation for the LC materials of positive and negative dielectric anisotropy, $\Delta\varepsilon > 0$ and $\Delta\varepsilon < 0$.

2. EXPERIMENTAL

2.1. Alignment Coatings

As the bounding substrates we used the following:

(1) polymer layers spin coated on glass slides (2×3 cm) from the polymer solution and subsequently backed. We used polyvinylcinnamate (PVCN) from Aldrich, polyimide (PI) 2555 from Dupont, polymethylmethacrylate (PMMA) from Aldrich. For VA we used PIs containing hydrophobic chains specially designed.
(2) bare glass substrates (microscope slides from Fisher Sci.).
(3) plasma coatings of hydrogenated carbon (a-C:H) prepared by plasma enhanced chemical vapor deposition as described in Ref. [14].

2.2. Irradiation Setup and Treatment Procedure

For irradiations, we used the ALT with a race track discharge channel (Fig. 1). This source worked in the regime of low energies ($E = 500$–$800\,eV$) and currents ($j = 6$–$15\,\mu A/cm^2$) [10]. The width of generated plasma "sheet" was about 30 cm. We characterized the beam intensity profile by scanning a probe parallel and across the "sheet" and measuring the ion current j. In the parallel direction, the beam is rather uniform. Across the "sheet", the j distribution is of Gaussian shape (Fig. 2, curve 1). Half-width of the beam intensity distribution corresponds to the cone of the angle $\beta \approx 6^\circ$ with the apex

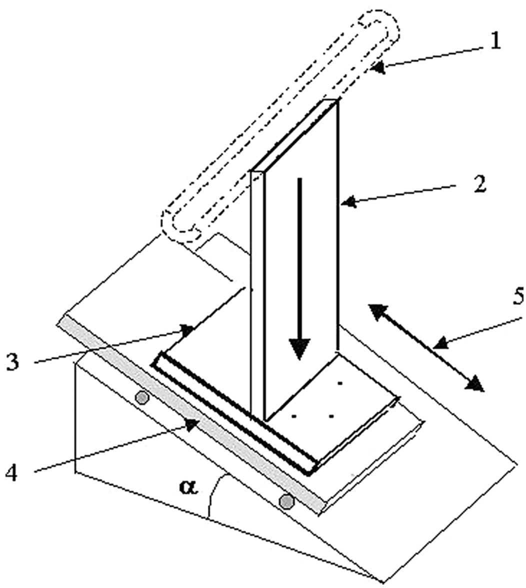

FIGURE 1 Sample irradiation geometry. 1) race track shaped discharge area; 2) plasma flux; 3) substrate; 4) translation system; 5) translation direction.

in the discharge area. The divergence of beam within this cone was further analyzed using the Faraday cup. The pinhole aperture of the cup was oriented perpendicularly to the beam propagation direction. The ion distribution behind the aperture was estimated by current measurement in the concentric rings made of copper wire mounted on the bottom of Faraday cup. This distribution is shown in Figure 2, curve 2. One can see that the majority of ions (>70%) travels within the cone with the half angle $\gamma \approx 3^\circ$. In other words, the particle beam is well collimated. However, some ions have path that diverges to rather large angles (>10°). As we will discuss later, this divergence might be responsible for generation of different modes.

The substrates were set for oblique irradiation. The distance between discharge area and treated substrates was varied within 6 and 25 cm. The substrate holder was mounted on the PC controlled translator providing translation in the sample plane perpendicularly to the plasma sheet, as shown in Figure 1. The translation amplitude was varied within 3–15 cm depending on the size of treated substrate and the translation speed was set at 2–5 mm/s. Due to the translation, different parts of the sample passed many times over the plasma beam undergoing alignment treatment (cycling dynamic regime).

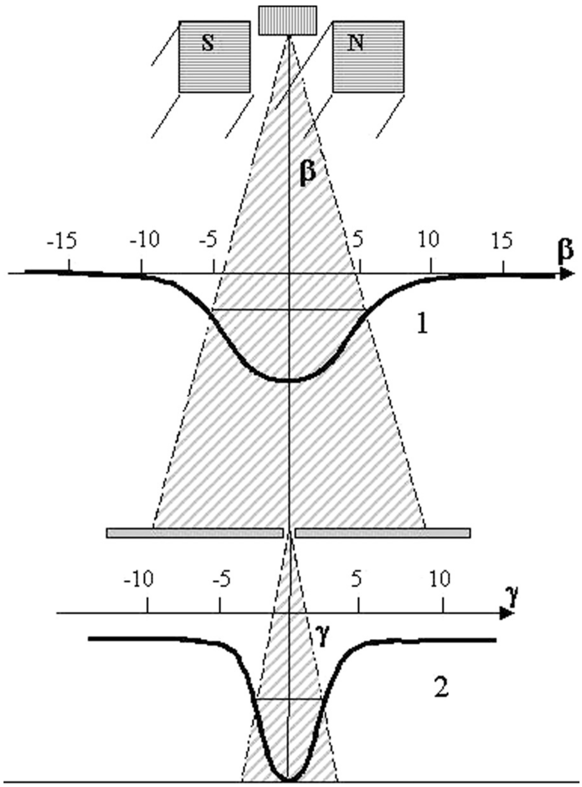

FIGURE 2 Scheme illustrating the beam profile (curve 1) and the beam divergence (curve 2).

Alternatively, the substrates were treated in the static irradiation regime. In this case, the sample was set in such a way that the most intensive part of plasma sheet corresponded to the middle of the treated substrate.

2.3. Cells

The LC alignment has been studied by preparing two types of LC cells: (1) one substrate is irradiated by plasma beam, while the second substrate has a rubbed polyimide layer (asymmetric cells); and (2) both substrates are irradiated with the plasma beam (symmetric cells). To obtain a uniform director orientation across the LC cell, the cells were assembled in an antiparallel fashion, meaning that the glass plates were set in such a way that the vectors specifying the direction of irradiation were antiparallel to each other. The asymmetric cells were prepared with the aim of determining the direction of LC alignment on the plasma treated substrate. The symmetric cells were used to measure the pretilt angle by crystal rotation method and magnetic null method. The cell gap was kept with spacers of 6 μm and 20 μm in diameter. As LC with $\Delta\varepsilon > 0$ we used nematic LC ZLI2293 purchased from Merck. As the LC with $\Delta\varepsilon < 0$ we used the nematic mixture MJ961180 (Merck Japan).

3. RESULTS AND DISCUSSION

3.1. Dynamic Irradiation Regime

Figure 3 shows two sets of asymmetric samples in which the tested PI substrate is treated in dynamic regime with the plasma beam ($j = 8\,\mu A/cm^2$, $E = 600\,eV$) over various periods of time. In the upper

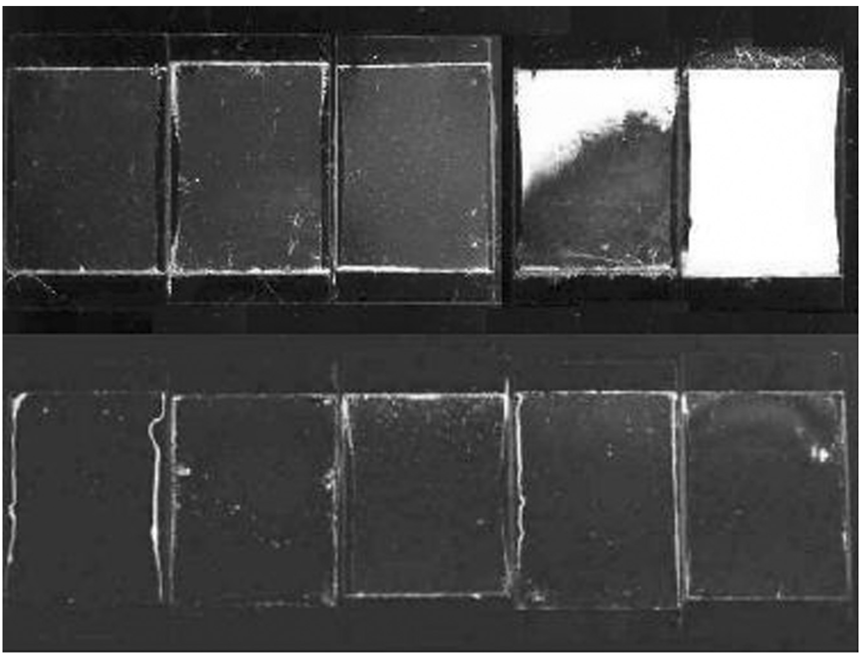

FIGURE 3 The set of asymmetric cells viewed between two crossed polarizers. The tested PI substrates in the cells have been irradiated during 1, 2, 4, 6, 10 min (set (a)), and 1, 2, 10, 20, 40 min (set (b)), respectively. Irradiation conditions: cycling regime, $\alpha = 70^\circ$, $j = 8\,\mu A/cm^2$, $E = 600\,eV$. The cells are filled with LC 5CB (set (a)) and MJ961180 (set (b)).

series, corresponding to ZLI2293 ($\Delta\varepsilon > 0$), the alignment transition from the 1st to the 2nd mode occurs at the irradiation time t_{exp} slightly longer then 5 min. Within 5 min and 8 min irradiation the sample contains areas with the 1st and the 2nd modes, i.e. the 1st and the 2nd mode coexist. No any transition types of alignment except coexisting 1st and 2nd modes are detected. Finally, at $t_{exp} > 10$ min only 2nd alignment mode is observed. The alignment characteristics in the 1st and in the 2nd mode as well as the methods of their controlling are described earlier in Ref. [8–11].

The lower set of samples in Figure 3 corresponds to LC MJ961180. Surprisingly, no transition from the 1st to the 2nd mode is observed, even for rather high irradiation times. The alignment in the 1st mode remains unchanged with the pretilt angle $\theta = 20^\circ$–30° that only weakly depends on the dose. The same trend was observed in alignment of $\Delta\varepsilon > 0$ and $\Delta\varepsilon < 0$ LCs on the obliquely deposited SiO_2 coatings. According to Ref. [15], at shallow-angle deposition, both LC with $\Delta\varepsilon > 0$ and LC with $\Delta\varepsilon < 0$ are aligned in the 1st mode. The difference is only in a value of pretilt angle, which is small ($\theta < 2^\circ$) for the LC with $\Delta\varepsilon > 0$ and high ($\theta = 87^\circ$–90°) for the LC with $\Delta\varepsilon < 0$. With the increase of the deposition angle (measured from the substrate), the LC with $\Delta\varepsilon > 0$ undergoes alignment transition from the 1st to the 2nd mode, while the LC with $\Delta\varepsilon < 0$ preserves the 1st mode of alignment. The planar or almost planar alignment of $\Delta\varepsilon > 0$ LC and homeotropic or almost homeotropic alignment of $\Delta\varepsilon < 0$ LC might be related to the different molecular (for example, dipole–dipole) interactions between the liquid crystal and the substrate, see Refs. [15–17] for the discussion of the current advances in the field. Although the detailed model of alignment is absent, it is clear that the dielectric anisotropy seems to be an important factor in the mechanisms of alignment at plasma-etched substrates, similar to alighnment on the SiO_2 aligning substrates.

By using the analogy with the obliquely deposited films one can explain the appearance of two alignment modes. In the case of obliquely deposited films the alignment transition from the 1st to the 2nd mode is explained by change of the surface profile. Tilted deposition results in formation of elongated surface features (needles, columns) tilted in the plane of deposition. Their growth results in merging of the individual needles and formation of rows elongated predominantly perpendicularly to the plane of incidence, according to a "self-shadowing" effect considered by Smith *et al*. [18]. Depending on the parameters of these features, the LC aligns along the needles (1st mode) or along the graves between the rows (2nd mode) in order to minimize the elastic energy.

The topographic features observed in plasma etching technique are somewhat similar to those detected for the films obtained by deposition; the elongated features aligned towards the direction of etching which merge in the rows perpendicular to the incidence plane of plasma beam with the increase of exposure dose [9–11]. The different modes of alignment might be caused by the effect similar to the self-shadowing effect, as the etched portions of the substrate with the slope along the direction of beam are less exposed to the flux. Apart from the self-shadowing effect, the topography changes observed in the AFM studies and manifested in the transformation of the 1st mode into the 2nd mode, might be also related to the finite divergence of the ALT plasma beam. The 2nd mode might be provoked by the ions that deviate from the average direction of deposition. The indirect evidence of this possibility comes from a rather surprising fact that the 2nd alignment mode was never described for the substrates treated obliquely with the ion beams generated by the Kaufman plasma source.

3.2. Static Irradiation Regime

In the static irradiation regime, the range of the observed alignment modes is wider than that obtained in the dynamic regime. Figure 4 shows two sets of asymmetric samples in which the tested PI substrate is treated in the static regime with the plasma beam ($j = 8\,\mu A/cm^2$, $E = 600\,eV$) over various periods of time. For LC ZLI2293 (upper set) one can observe alignment in the 1st ($t_{exp} < 3\,min$) and in the 2nd mode ($t_{exp} > 5\,min$)over the whole substrate and the alignment transition from the 1st to the 2nd mode between 3 and 5 min of irradiation. The analysis of samples with coexisting modes suggests that the 2nd mode first appears in the area most intensively treated with plasma (the central part of the beam, curve 1 in Fig. 2). This is in agreement with the fact that the 1st–2nd mode transition is triggered by the increase of irradiation dose.

In the LC MJ961180 (lower set in Fig. 4) one can also observe alignment in the 1st and in the 2nd mode. However, while the 1st mode alignment can be obtained over the whole substrate ($t_{exp} < 7\,min$), the 2nd mode alignment over the whole substrate was not achieved even for high irradiation doses corresponding to complete etching of the aligning film. It becomes apparent only in the central, most intensive part, of plasma “sheet” at the irradiation doses 2–3 times higher than the doses needed for the 2nd mode alignment of LC ZLI2293. It is not completely clear now why this mode appears only in a static regime.

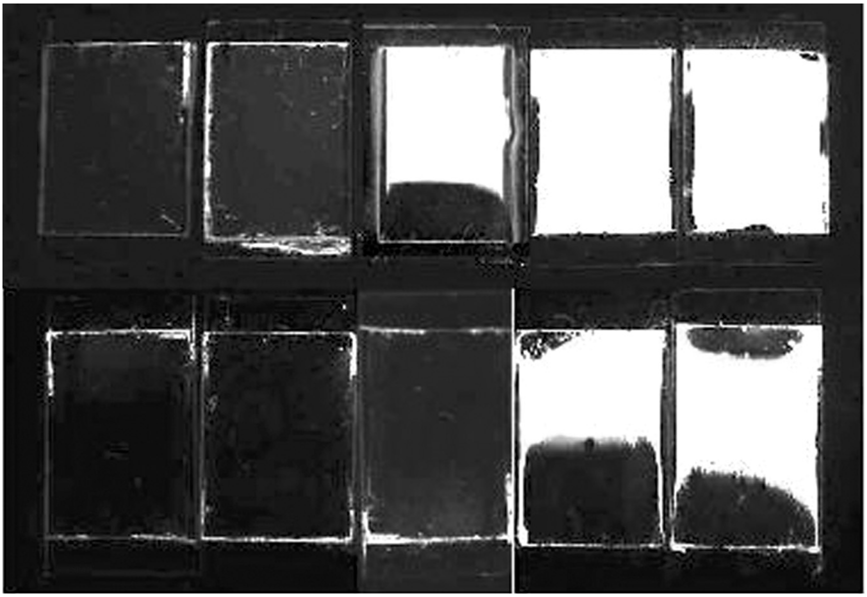

FIGURE 4 Photos of asymmetric cells (d = 20 μm) viewed between a pair of crossed polarizers. The cells are filled with LC 5CB (set (a)) and MJ961180 (set (b)). In each set, the tested PI substrate is treated with plasma beam over 1, 3, 5, 15, and 30 min in static regime.

Considering the cells with coexisting alignment modes one can observe that the area aligned in the 1st and 2nd mode are separated by narrow transition areas. The narrow size of these transition areas implies that the range of doses corresponding to their realization is rather narrow. The necessary dose can be achieved in the static regime, because of continuous intensity distribution in the sample plane determined by the transversal shape of plasma "sheet" and distance from the discharge area. At the same time, it is difficult to fall into this range in case of dynamic irradiation.

As can be seen from Figure 5, the transition areas are characterized by multidomain LC alignment. The easy axis in these domains is rotated symmetrically by about $\pm 45^\circ$ with respect to the alignment direction in the 1st mode area (two-fold degenerate alignment). This kind of transition alignment was earlier observed for the obliquely deposited SiO_2 substrates [19], as well for photoaligning substrates [20], and seems to be general for LC alignment transitions characterized by 90° reorientation of the LC easy axis.

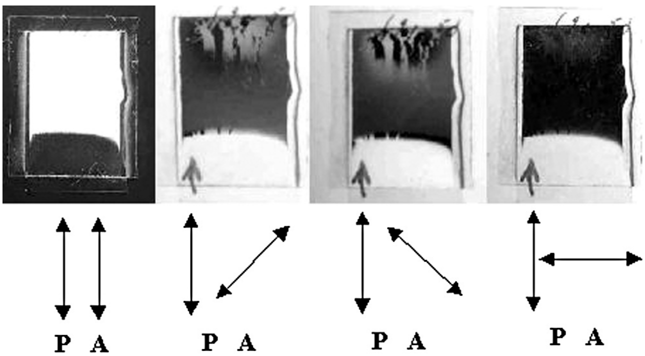

FIGURE 5 The photos of asymmetric cell viewed between polarizer and analyzer. The position of polarizer and analyzer is schematically shown below each photograph.

This is noteworthy to notice that the features described above are general for all aligning materials (of the organic and inorganic origin) used in the present research. This gives us one more reason to believe that both the topographic factor and symmetry of molecular interaction at the LC – plasma-treated substrate interface are responsible for the observed alignment features.

3.3. LC Alignment at the Extremely Low Irradiation Doses

In this regime we reduced the current density to $j < 0.5\,\mu A/cm^2$ and used a short irradiation time (5–15 s). This irradiation dose was sufficient to induce 1st mode alignment in a big number of material of the organic origin. The induced pretilt angle was low ($<3^\circ$) except the hydrophobic chains containing polyimides specially developed. These PIs provided homeotropic alignment of both LC ZLI2293 and LC MJ961180 before any treatment and high pretilt LC alignment ($\theta = 87^\circ$–90°) after the plasma treatment with a low irradiation dose. This result shows that plasma alignment method can be successfully used to realize vertical alignment LCD mode. We observed the transition from the high tilt alignment to the low tilt alignment with the increase of irradiation dose, similarly to that which was earlier observed for the photoalignment procedure [21,22]. This alignment transition is probably caused by the destruction of hydrophobic chains with a plasma beam. The further increase of irradiation dose resulted in the transition to the 2nd mode, as in the other alignment films. The high tilt alignment and the following sequence of the alignment transitions described above were observed for both static and dynamic irradiation regimes.

4. CONCLUSIONS

On the substrates obliquely treated with a plasma flux we have experimentally found two modes of planar/tilted LC alignment with the easy axis confined to the plane of plasma incidence (mode 1) or perpendicular to this plane (mode 2). In the 1st alignment mode the LC pretilt angle is non-zero and can be varied with the irradiation conditions, while in the 2nd mode the pretilt angle is zero. The two-mode alignment can be explained assuming a change in surface topology caused by irradiation. With the increase of irradiation dose (the product of current density and irradiation time), the alignment transition from the 1st to the 2nd mode occurs. Between the 1st and 2nd alignment modes the transient two-fold degenerate type of alignment can be observed. The sequence of the alignment types 1st mode – two-fold degenerate alignment – 2nd mode is observed for both LC with $\Delta\varepsilon > 0$ and $\Delta\varepsilon < 0$. This sequence is similar to transformations observed earlier for the aligning substrates obtained by oblique deposition [19] and photoalignment [20]. Finally, we note that the present alignment technique is of great practical interest for display industry, as describe in refs. [8–11,14,21,22]. In the present paper we additionally show that it can be extended for the case of vertical alignment extensively used in the modern LCD.

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