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The rubbing supplemented atmospheric plasma process for tunable liquid crystal alignment

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ABSTRACT

Processing of the liquid crystal (LC) aligning substrates by a flux of atmospheric plasma provides controllable pretilt angle and anchoring energy, but rather poor alignment uniformity on macroscopic scale. The result is however radically improved by combination of this process with rubbing. In this case, high-quality tilted alignment is realized with a pretilt angle continuously tuned in the range 0–90°. The corresponding cells show excellent electro-optic performance. This makes combination of atmospheric plasma and rubbing processes rather attractive for industry, especially for those cases where the LC pretilt angle and anchoring energy should be patterned or continuously tuned.

1. Introduction

Perfection of liquid crystal (LC) devices and extension of the area of their applications strengthen demands to LC alignment. These demands include high alignment uniformity, adjustable pretilt angle and anchoring strength, easy pattering procedure, and high alignment stability. Besides, the range of alignment parameters should be substantially broadened and some uncommon combinations of these parameters are sometimes required. The conventional rubbing technique is unable to satisfy perfectly all these demands. However, some of them can be met by using alternative alignment processes, such as photoalignment [1], vapor [2,3] and ion beam sputtering deposition [4,5], ion [6–8] and plasma beam alignment [9–11]. The ion and plasma beam alignment procedures currently attract especial interests. They are effective for various classes of LCs, provide very high alignment uniformity, full range control of pretilt angle, and easy way for alignment pattering. Wide practical application of these processes is mainly hindered by a high vacuum (10^{-6}–10^{-5} Torr) operation. To realize this regime, expensive vacuum equipment is necessary. Besides, this process consumes essential time, first of all, because of partial or full depressurization of working area required for reloading of aligning substrates. These difficulties can be circumvented by transferring the process to the range of atmospheric pressures.

The first attempts in this direction were recently made. LC alignment of rather good *microscopic* uniformity with controllable pretilt angle was realized by processing the aligning substrates with a stream of atmospheric plasma (AP) from barrier [12] and jet [13,14] discharges. The uniformity of this alignment on *macroscopic* level was not discussed. However, parameters of generated plasma fluxes and low switching contrast of fabricated cells indicated that macroscopic uniformity was insufficiently good.

The goal of the present paper is to make a deeper insight into the AP process for LC alignment and bring it closer to industrial applications. It is demonstrated that the alignment capability of this process is dramatically increased when one combines it with a conventional rubbing or other process yielding sufficient alignment uniformity in plane of LC cells. The effect of atmospheric plasma on the aligning layers and thereby LC alignment has been also investigated.

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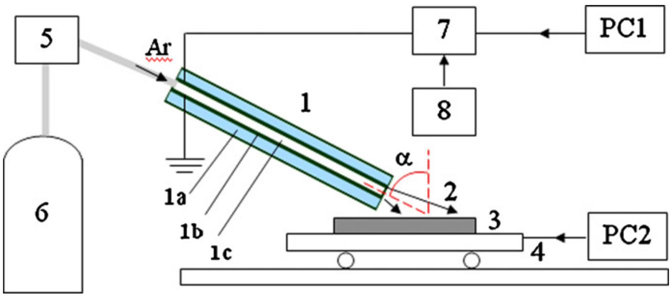

Fig. 1. Diagram of atmospheric plasma processing setup. 1 – barrier discharge block (1a – glass plate, 1b – ITO electrode, 1c – discharge area), 2 – flow of active particles, 3 – substrate, 4 – moving system, 5 – gas feed regulation system, 6 – gas cylinder, 7 – gas parameters measuring block, and 8 – power supply.

2. Experimental

Similarly to [12], our AP processing setup was based on the barrier discharge. However, in contrast to glow barrier discharge [12], classical, filamentary type, barrier discharge was employed. It consists of numerous microdischarges with duration of tens of nanoseconds and diameter of the order of 0.1 mm. This type of discharge can be initiated in practically any gaseous medium at frequency of the supply voltage from tens of hertz to hundreds of kilohertz [15].

A schematic diagram of the used set up is presented in Fig. 1. The barrier discharge was initiated in the narrow gap (d = 1 mm) 1 between two parallel flat electrodes subjected to high alternating voltage (10–15 kV, 400 Hz). The gap was filled by argon. The active particles 2 were extracted from the discharge area by the gas expulsion. The volume velocity of the gas was varied by a gas feed system 5 in the range 0.1–10 l/min. The gas stream with the involved active particles was directed to the glass/ITO substrates 3 containing polyimide coating on the top. The distance between the plasma nozzle and the substrate was about 3 mm and the angle α between the substrate's normal and the stream direction was about 60°. The substrates were mounted on the moving platform 4 translated forward and backwards under the particle stream with a speed of 2 mm/s. The processing dose was varied by changing discharge power, gas stream velocity and number of scans. The time period between the plasma processing and cell assembling was shorter then 2 h.

The aligning layers were the films of polyimides AL2021 (JSR, Japan) and SE3510 (Nissan, Japan) designed, correspondingly, for vertical and planar alignment. These films were spin coated on the glass/ITO slides, appropriately backed and subjected to atmospheric plasma treatment. Two series of cells were investigated. In the first series the substrates of the cells were subjected to only AP treatment. In the second series, the AP processed substrates were additionally subjected to rubbing. The substrates were unidirectionally rubbed with a velvet cloth with a force of 20 N/cm^2 over a distance of 30 cm with a velocity of 10 cm/s. The rubbing direction was parallel to the projection of plasma flux on the substrate in a course of treatment.

The cells were assembled from two equally treated substrates combined in such a way that their rubbing/plasma processing directions were antiparallel. A cell gap was maintained by 18 μm and 6 μm spacers. The cells were filled with nematic LCs MJ961180 (Merck Japan) and E7 (Merck) designed for VA and TN mode, respectively. The quality of LC alignment was monitored by observation of the cells placed between two crossed polarizers, both by naked eye and with an optical polarizing microscope. The pretilt angle in the cells, θ, was measured by a conventional crystal rotation method, while the polar anchoring coefficient, W_p, was estimated by modified Yokoyama and van Sprang technique [16]. The electro-optical measurements were carried out be using original setup described in [17]. The AFM measurements were carried out by scanning atom force microscope Nanoscope IIIa from Digital Instruments working in a tapping mode.

3. Results and discussion

At first we characterized alignment on the substrates treated solely by AP stream. Fig. 2(a) demonstrates a set of corresponding AL2021/MJ961180 samples. A low dose exposure induces just a slight deviation of LC alignment from the homeotropic state (90° > θ >88°) towards incidence direction of AP stream without noticeable alignment degradation. The further increase of the exposure dose results in transition from the high-pretilt angle to the low-pretilt angle state with insufficient alignment uniformity (cell 4, Fig. 2). Even the cells with better alignment (cells 2 and 3 in Fig. 2) demonstrate non-uniform homeotropic-to-planar reorientation under the applied voltage (Fig. 3(a)). The LC alignment on the planar polyimide SE3510 was also of rather poor macroscopic uniformity in a broad range of exposure doses.

These results sharply contrast with the results for the high-vacuum process yielding very uniform planar/tilted LC alignment [6–11]. This difference can be explained by different degree of collimation of particle beams, which determines anisotropy of treatment. In the high vacuum case, mean free path of active particles l is rather big (l > 10 cm [18]) that results in good collimation of the particle beams. At atmospheric pressure the mean free path l is considerably shorter (l < 1 μm [18]), because active particles intensively collide with molecules of atmosphere giving rise to the secondary active particles with random directions of movement. This results in strong divergence of the active particle beam. Besides, experiencing many collisions before entering the aligning layers the primer particles lose energy that weakens their treatment potential. These factors determine poor anisotropy of treated surfaces.

Thus, a sole atmospheric plasma treatment does not provide acceptable planar and tilted alignment of LC. Because of this, we switched over to the combination of AP processing and conventional rubbing believing that the first action will provide control of pretilt angle and anchoring energy, while the second one will cause alignment uniformity. A similar approach was earlier applied to realize LC alignment on the substrates treated in vacuum plasma discharges [19,20]. Both sequences of AP and rubbing processes have been tested. Below is however considered only the order

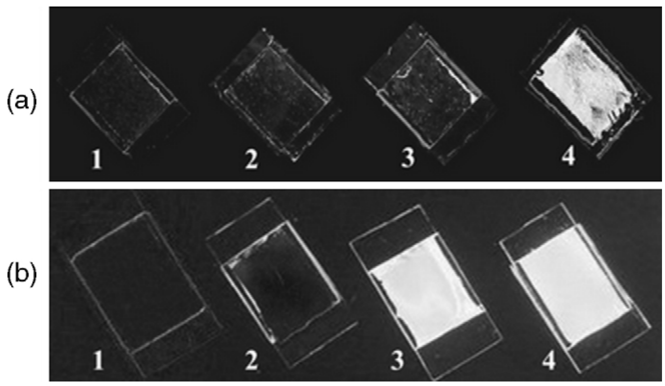

Fig. 2. Photographs of LC cells based on (a) AP processed and (b) AP and rubbing processed aligning layers of polyimide AL2021. The cells are filled with LC MJ961180 and placed between a pair of crossed polarizers so that the directions of AP/rubbing treatment of the aligning substrates form an angle 45° with the directions of the polarizers. In each series, the cells differ in a number of scans of aligning layers, N. In (a) series, N = 0, 2, 4 and 12, while in (b) series N = 0, 2, 6 and 12, for the cells 1, 2, 3, and 4, respectively. The discharge power is 4 W and the stream velocity is 9 l/min.

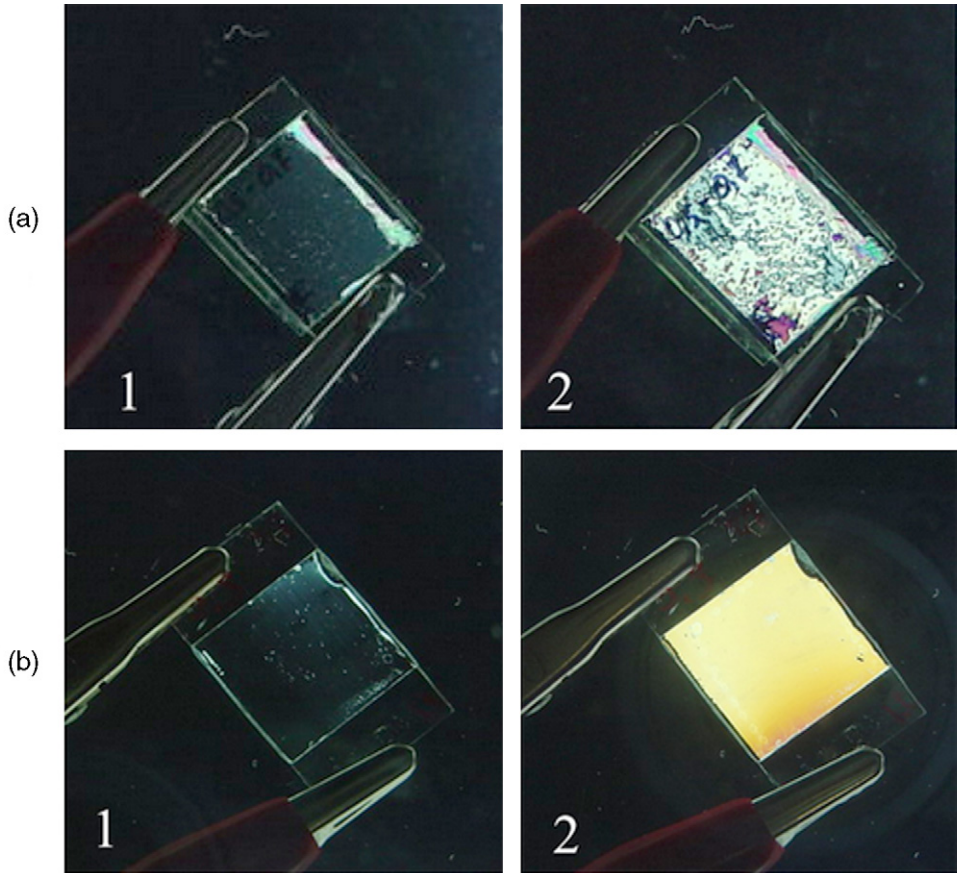

Fig. 3. Photographs of LC cells based on polyimide AL2021 aligning films (1) before and (2) during application of electric field of 6 V. The polyimide substrates are processed by AP plasma in case (a) and AP and rubbing in case (b). The cells are filled with LC MJ961180 and placed between a pair of crossed polarizers so that the angle between the AP/rubbing treatment direction and the directions of the polarizers is about 45°. The AP processing parameters are 4 W, 9 l/min, 4 and 2 scans, respectively.

AP–rubbing, which appeared to be much effective for the LC alignment.

Combining AP and rubbing treatment we realized uniform LC alignment on both homeotropic and planar type polyimides. By way of example, Fig. 2(b) demonstrates a set of cells based on AL2021 aligning layers filled with LC MJ961180. There is evident that quality of LC alignment is rather good in a wide range of exposure doses.

In Fig. 4 the pretilt angle θ in the cells based on AL2021 and SE3510 polyimides is plotted as a function of number of scans *N*. As is obvious, θ continuously decreases with *N*. In case of homeotropic polyimide AL2021 it runs from 90° to about 0°, *i.e.*, is controllable in a full range of this parameter. For the SE3510/E7 couple we also investigated dependence of polar anchoring coefficient, W_p, on the AP dose. It was realized that W_p grows with the dose showing tendency of saturation. For instance, for the SE3510 layers solely rubbed W_p was equal to 1.3×10^{-3} J/m^2, while for the layers subjected to both AP plasma (4 W, 9 l/s, 6 scans) and rubbing it was 4.8×10^{-3} J/m^2. Note that similar trends were obtained by changing the exposure dose via varying the power of discharge and gas stream velocity.

The cells produced by combination of AP processing and rubbing demonstrate good electro-optic performance. Fig. 4(b) shows AL2021/MJ961180 sample with a vertical alignment in the field off and on states. As is obvious, LC layer uniformly switches in the electric field. The corresponding transmittance *T* vs. voltage *U* curves are given in Fig. 5. As expected, the pretilt angle decrease results in lowering of electro-optic contrast and, simultaneously, lowering of controlling voltage. Thus, providing continuous control of pretilt angle and anchoring strength, the proposed method enables to optimize the electro-optic performance of LC cells.

Finally, we consider microscopic mechanisms of LC alignment on the AP treated surfaces. The major discussing point was continuous decrease of the LC pretilt angle with the exposure dose (Fig. 4). It was reasonable to assume that, similarly to the case of high vacuum plasma [19,20], this decrease is caused by destruction of hydrophobic chains on the surface of aligning film. To clarify this, wetting

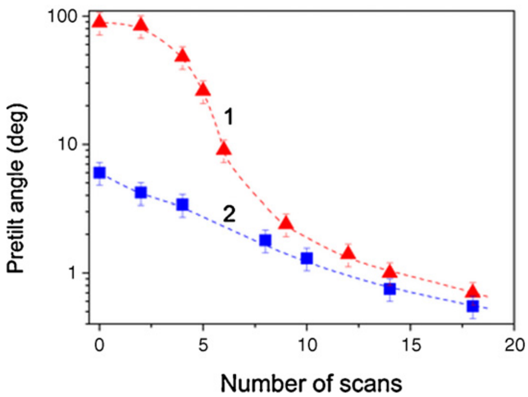

Fig. 4. LC pretilt angle as a function of number of scans for the polyimide layers processed by AP stream (4 W, 9 l/min) and subsequently rubbed. Curves 1 and 2 correspond to pairs MJ961180/AL2021 and E7/SE3510, respectively. The curve for other pair E7/AL2021 is rather similar to curve 1. The lines are just for eye guidance.

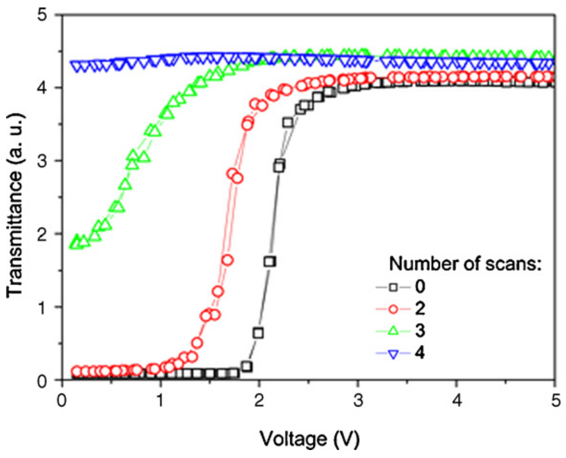

Fig. 5. Transmittance vs. voltage curves for the set of cells based on AP processed and rubbed aligning films of polyimide AL2021. Plasma processing parameters are 4 W and 9 l/min. The number of scans is varied.

properties of the treated surfaces have been investigated. The contact angle values for distilled water and α-bromonaphthalene, two well characterized liquids, were measured at room temperature in air by the sessile drop technique. The obtained data were used to calculate surface free energy for the treated polyimide layers by Owens's formula [21]. According to Fig. 6(a), surface free energy quasilinearly grows with an exposure dose. Comparing Fig. 6(a) and Fig. 4 one can notice that the LC pretilt angle monotonically decreases with a free energy of the aligning surface. This agrees well with other observations [22,23]. Besides, these data are in good agreement with Kreagh and Kmets [24] energy criterion predicting type of LC alignment based on the difference of surface free energies of LC (γ_{LC}) and aligning layer (γ_{AL}). According to this criterion, planar alignment arises at $\gamma_{LC} - \gamma_{AL} < 0$, and homeotropic alignment at $\gamma_{LC} - \gamma_{AL} > 0$. For nematic LCs, γ_{LC} usually falls in the range 30–35 mJ/m^2 [25,26] that corresponds to middle of the range of γ_{AL} realized in the plasma process (see Fig. 6(a)). This means that the discussed criterion predicts anchoring transition from homeotropic to planar alignment with the plasma exposure dose, which is indeed experimentally realized.

Growing of surface free energy of the aligning layers with the exposure dose implies that hydrophobicity of these layers becomes weaker. This in turn suggests that the treated surfaces lose hydrophobic fragments. Such conclusion was subsequently supported by AFM measurements. As is evident from Fig. 6(b), the AP treatment reduces amount of "hillocks" on the aligning surface associated with the self-assembled hydrophobic chains. The Fourier transformation of the AFM images did not reveal surface anisotropy of the treated films that agrees with a poor LC alignment on these films.

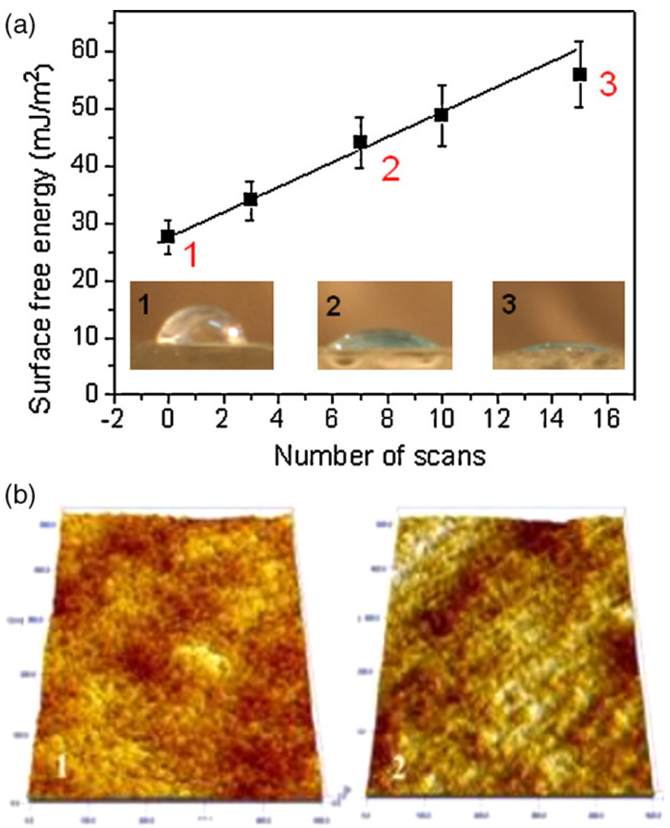

Fig. 6. (a) Surface free energy of AL2021 film subjected to AP treatment (3 W, 9 l/min) as a function of number of scans. The inset shows the photos of water drops corresponding to several exposure doses. (b) AFM images of polyimide AL2021 film (1) before and (2) after treatment with atmospheric plasma (4 W, 9 l/min, 8 scans). The scanned area is 5 μm × 5 μm.

4. Conclusions

In summary, the alignment effect of atmospheric plasma stream can be dramatically improved by its combination with a conventional rubbing or, presumably, other process generating good alignment uniformity in plane of aligning films. In this case, the advantages of AP treatment and rubbing are beneficially combined; the plasma process is used to set desirable value of pretilt angle (via controlling of surface density of hydrophobic chains), while the rubbing provides alignment uniformity (via effective generation of surface anisotropy). Combination of these processes yields a wide-range controlling of pretilt angle and anchoring energy for the same aligning material. The rubbing supplemented AP processing can be quite easily introduced in a manufacturing of LC devices, because it is compatible with the in-line and roll-to-roll modern manufacturing principles and predicts just inessential and cheap modification of the currently used production lines.

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