32.4: Two Modes of LC Parallel Alignment on the Plasma Treated Substrates

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Abstract
We propose a new alignment procedure for liquid crystals cells that yields both zero and non-zero pretilt. This procedure is an oblique irradiation of the bounding substrates with the directed plasma flux. As a source of plasma irradiation we use an anode layer thruster producing sheet like plasma fluxes suitable to treat large-area substrates. Both organic (polymers) and inorganic (glass, ITO) layers can be treated. Plasma beam irradiation results in two types of LC alignment: (1) the easy axis in the incident plane formed by the direction of beam and the normal to substrate; (2) the easy axis perpendicular to the plane of incidence. By increasing the irradiation dose, one can change the alignment direction from the type (1) towards the type (2). In the first type of alignment, the pretilt angle can be controlled by changing parameters such as irradiation angle, ion current density, ion energy, etc. The second type of alignment is characterized by a zero pretilt. The azimutal anchoring energy coefficient is relatively weak ($W=10^{-3}$ erg/cm^2) for the first type of alignment and strong ($W>10^{-1}$ erg/cm^2, comparable to the rubbed polymer substrates) for the second type. The two-mode alignment feature can be used to generate alignment with desirable parameters as well as to pattern the LC cell substrates. The method is free of certain shortcomings known for the traditional rubbing technique.

1. Introduction
Uniform alignment is a key problem in practical applications of liquid crystals (LC). Usually, parallel alignment is required if an electric field is applied across a cell filled with a LC of a positive dielectric anisotropy. In this mode, the LC director is switched between parallel to perpendicular (with respect to the substrates) orientations. In some operating modes, LC alignment might be required to be tilted (non-zero pretilt angle).

The prevailing technique of parallel alignment is rubbing of polymer films deposited onto the substrates. This method suffers from some drawbacks. The rubbing process causes surface deterioration as well as generation of electrostatic charges and dust on the aligning surfaces. As the technique implies a direct mechanical contact with the treated substrate, it is often hard to use when one needs a non-trivial alignment pattern, for example, in the so-called multidomain alignment. Over the last decade, a number of non-contact LC alignment methods has been suggested. Among them the photoalignment method is the most promising and studied [1]. However, the photoaligning technique is usually accompanied with a low anchoring strength and relatively poor photo and thermal stability. This seems to be caused by relatively weak changes that a UV/visible beam can inflict upon the treated substrate. To strengthen the aligning action, a deep UV treatment was also suggested.

Another approach to non-mechanical alignment is irradiation with particle beams. To generate surface anisotropy sufficient for planar LC alignment, the substrates are irradiated with particle beams using two different types of techniques. In the first technique, the beams are to deposit the aligning film onto the bare substrate. The deposition might be direct (plasma enhanced chemical vapor deposition, etc.) [2] or indirect (ion beam sputtering, etc.) [3]. In the type of treatment, the beam is used to etch the aligning material that was deposited prior to irradiation. M.J. Little et al. [4] suggested oblique irradiation of the aligning films with the ion fluxes of high energy (1-3 keV). Recently, the IBM group modified this procedure by using low energy ions (50-300 eV) [5,6]; the ion source is of Kaufman type. The principal advantage of this innovation is that the ion beam affects only the very top layer of the aligning film. This feature helps to mitigate generation of free radicals, which worsen performance of LC displays (LCDs). According to [5,6], the method provides excellent LC alignment on both organic and inorganic substrates.

In this work, we describe another type of ion source, an anode layer thruster, and characterize alignment of typical LCs at different substrates treated with plasma this source generates. Using treatment parameters similar to those in [5,6], we achieve two modes of parallel LC alignment with different geometrical (easy axis direction) and energetic (strength of azimuthal anchoring) properties.

2. Experimental

2.1 Ion source and Irradiation Procedure
The irradiation set up is based on anode layer thruster (ALT) specially designed to produce collimated flux of ions from practically any gaseous feed. The ALT belongs to the class of closed drift thrusters (CDTs). This sort of thrusters has been optimized in former SU for high thrust efficiency (>50%) to use on satellites for the near-term propulsion. This type of sources is also used in a variety of plasma etching and plasma deposition systems.

As compared to electrostatic ion thrusters, the closed drift thrusters have a simpler construction. They do not require filaments or secondary electron sources to initiate discharge current or to neutralize the beam. Since the ions in CDTs are accelerated electrodynamically, the grids to extract and accelerate ions are not needed. The CDTs have long lifetime, high efficiency and thrust density (unlike the electrostatic ion thrusters, CDTs are not space-charge limited).

A scheme of the anode layer thruster is shown in Fig. 1. The source has permanent magnets at the inner and outer cathodes.

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The anode is above the inner and outer cathodes. Together these electrodes define the size and the shape of the discharge channel. The ion flux is formed in crossed electric (**E**) and magnetic (**H**) fields immediately within the discharge channel and thus it is a part of d.c. plasma generated in the discharge area. The details of construction, characteristics and principles of operation of this device can be found elsewhere [7].

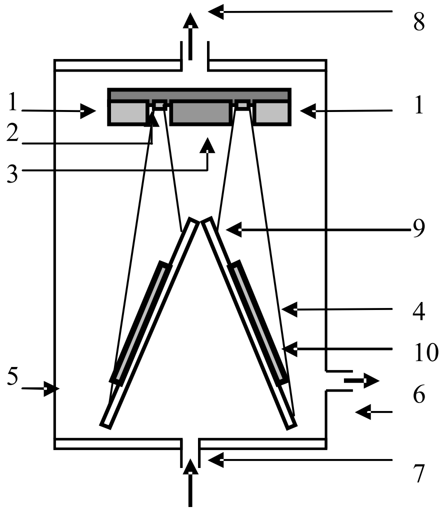

Figure 1. Scheme of anode layer thruster and irradiation method. 1-outher cathode and N pole; 2 - anode; 3 - inner cathode and S pole; 4 - plasma flux; 5 - body of vacuum chamber; 6-8 – gas valves; 9 – substrate holder; 10 – substrate.

Depending on the configuration of the discharge channel, the generated plasma fluxes have a shape of a hollow cylinder or a sheet. The latter one is suitable to treat large-area surfaces (by tilting or translating the sample).

We used the anode layer thruster with the race track shape of the discharge channel and argon as a working gas. The Ar^+ ions caused non-reactive etching of the aligning substrate. The pressure P in the source chamber was (2-10) 10^{-4} Torr. It determined current density j of Ar^+ ions. The ion energy was controlled by the anode potential U. It was varied within the range 200-1000 eV. The following three parameters of plasma irradiation were independently varied in our experiments: 1) irradiation time τ_{exp}; 2) current density j; 3) ion energy E.

The substrate holder was mounted in a vacuum chamber just under the discharge channel (Fig. 1). The distance between the plasma outlet and the irradiated substrate was about 6 cm. The substrates were irradiated slantwise. The plasma beam incidence angle α was varied between 0^0 (normal to the substrate) and 80^0. To create patterns of irradiation, we used paper and plastic masks being in contact with the substrates.

2.2 Samples

We used many organic and inorganic materials to prepare aligning films for LC cells. Among polymers, we tested the polyimide PI 2555 purchased from Dupont, polyvinylcinnamate (PVCN) from Aldrich, polymethylmethacrylate (PMMA) from Aldrich and others. The polymers were dissolved in an appropriate solvent and spin coated on the glass plates over ITO electrodes. After that, the substrates were baked to remove solvent. We also used films of a-C:H plasma polymer deposited by plasma enhanced chemical vapor deposition. As inorganic substrates, we used bare glass slides (microscope slides purchased from Fisher Scientific) and ITO coated glass slides. The irradiation conditions were optimized for each type of substrates.

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 asymmetric cells with twist director configurations were used to estimate the azimuthal anchoring coefficient. The symmetric cells were used to measure the pretilt angle by crystal rotation method. The cell gap was kept with spacers of 6 μm and 20 μm in diameter. The cells were filled with the nematic LC K15 (5CB) and ZLI4801-000 purchased from Merck.

3. Results and Discussion

3.1 LC alignment

A uniform parallel alignment of the nematic director in the cells with the plasma treated substrates is observed for a wide range of irradiation parameters: j= (0.5-30) $\mu A/cm^2$, E= (200-1000) eV, τ_{exp}= 0.1 – 20 min. We have observed two modes of uniform LC alignment with different easy axis orientation. In the first mode, the easy axis is in the incident plane formed by the direction of beam and the normal to substrate. In the second mode, the easy axis is perpendicular to the plane of incidence. Figure 2 shows that the transition from the 1^{st} mode to the 2^{nd} mode is caused by the increase of irradiation time. A similar transition from the 1^{st} mode to the 2^{nd} mode is observed when one increases the current density of the argon ions. In other words, the type of alignment is controlled by the irradiation dose. Note that the two modes of alignment are apparently absent in the technique proposed by the IBM group [5, 6].

3.1.1. Alignment mode 1.

The typical sample aligned in the 1^{st} mode is shown in Fig. 3a. This alignment mode is characterized by a non-zero pretilt angle. The LC tilts in the direction of plasma beam incidence. The value of pretilt angle can be controlled within a relatively broad range ($0^0<\theta<10^0$) by changing the irradiation parameters. Figure 4 shows how the pretilt angle θ changes with the plasma beam incidence angle α; the dependencies are presented for different aligning films. These functions $\theta(\alpha)$ are non-monotonous with the maximum at α=40°-50°. The pretilt angle also depends on the ion current and the ion energy [8]. The azimuth anchoring energy W_a in the 1st mode of alignment has been estimated to be of the order of 10^{-3} erg/cm^2. This value corresponds to a relatively weak anchoring. The 1^{st} mode of alignment is close to the alignment mode reported by the IBM group [5,6] with that exception that the azimuthal anchoring coefficient W_a in our case is relatively low. Other parameters of the 1^{st} mode of alignment can be found in Refs. [8, 9].

3.1.2. Alignment mode 2.
The LC cell aligned in the 2nd mode is shown in Fig.3b. This mode is characterized by a zero pretilt. A non-zero pretilt can be generated by subsequent irradiation of the substrate originally aligned in the 2nd mode. The azimuthal anchoring coefficient corresponding to the 2nd mode is high ($W_a \geq 0.5$ erg/cm^2). This estimate is independently confirmed by a method described in [10]. These values of W_a are comparable to the values usually reported for rubbed polymer aligning substrates. The LC alignment of the 2nd type has been described for some photoaligning processes and for the obliquely sputtered SiO_x films [11] but not for the technique of plasma etching.

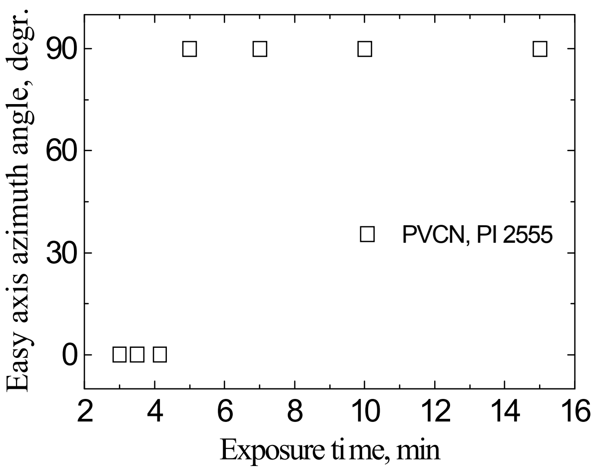

Figure 2. Azimuthal angle of the LC easy axis at plasma treated PI substrate as a function of irradiation time. The data are practically the same for 5CB and ZLI 4801-000 nematic LCs.

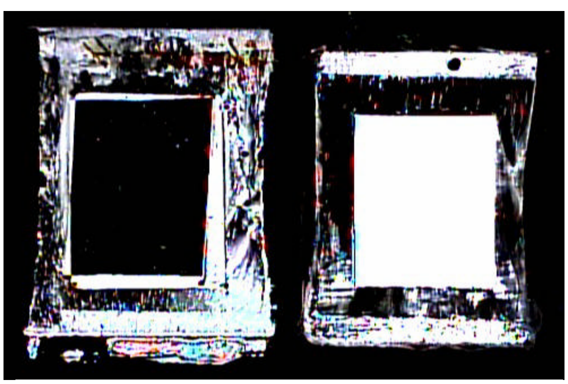

Figure 3. Photos of two combined cells filled with LC 5CB having rubbed PI substrate as a reference substrate and plasma treated glass slide as an object substrate. The object substrates are irradiated through the mask opening rectangular area in the middle of the substrate. The cells are placed between pare of crossed polarizers. The photos exhibit LC alignment in mode 1 (a) and mode 2 (b).

3.1.3. Alignment stability.
In order to check the thermal stability of LC alignment at the plasma treated substrates, the cells were exposed to 90^0 C over 3 hours. The heating treatment did not cause any substantial change of alignment quality for both alignment modes. The induced alignment is also photo-resistant; we did not observe any deterioration of LC alignment after irradiation of our cells with unpolarized UV light (15 mW/cm^2, 1 hour). At the same time, stability of the LC pretilt angle substantially depends on material of the aligning film. For some polymer coatings, a decrease of the LC pretilt angle was detected. The time of this decrease was about two weeks. This can be explained by the appearance of low-molecular weight products of plasma etching, which can be dissolved in the LC. However, the pretilt angle values can be stabilized by selecting proper materials for the aligning films.

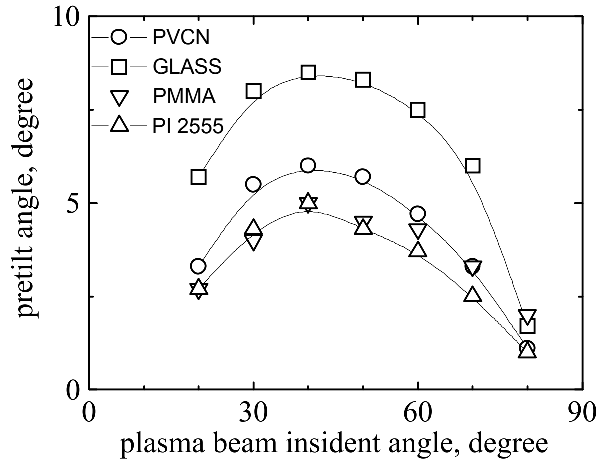

Figure 4. The dependency of LC pretilt angle vs plasma beam incidence angle measured for different substrates. The irradiation parameters for polymer and glass substrates are j=8μA/cm^2, E=600 eV, τ_{exp}=1.5 min and j= 2 μA/cm^2, E=500 eV, τ_{exp}=1.5 min respectively. The cells gap is 20 μm.

3.1.4. Patterning.
The two-mode alignment opens new opportunities for the patterning of the LC alignment. For instance, two-domain azimuthal patterning can be realized by one masking step without any rotation of the substrate.

3.1.5. Electro-optic performance.
The light transmission T vs applied voltage V curves have been measured for TN cells aligned by plasma alignment method. The obtained T-V curves are very similar for those for the cells prepared with rubbing alignment [8]. In addition, we did not observe any substantial difference in dielectric properties of LC materials aligned by these two methods.

3.2. LC alignment mechanisms
The nature of LC alignment at different substrates depends on the variety of factors. One of the most important factors is the direct anisotropic interaction between the molecules of two adjacent media; it a hypothetical case of an absolutely flat interface, this

interaction would be responsible for the LC alignment. It can be called an epitaxial factor. Another factor is topographical and related to the intrinsic elasticity of the LC: if the LC is in contact with a non-flat substrate or in a non-flat sample, it will align along the direction (or directions) that yield the smallest energy of elastic distortions.

As indicated in Ref. [5,6] the anisotropy of direct molecular interactions plays an important role in the LC alignment at the plasma etched substrates. To clarify whether the topographic factor might be important, we studied the surface profile of the plasma treated substrates by atomic force microscopy (AFM Nanoscope IIIa). According to these results, the surface of plasma-treated plates becomes rougher as compared to un-treated substrates. At the treated substrates, one can often distinguish topographical features of the average size 10-100 nm. In many cases, these features have an elongated shape and some degree of orientational ordering (Fig. 5). It appears that the direction along which the surface profile is the smoothest is the easy axis of LC alignment. By setting geometrical parameters of surface undulations, namely, the amplitude a = 0.4-1 nm and the wavelength $\Lambda = 10 - 50$ nm in the Berreman formula,

$$W_a = \frac{1}{2} K a^2 \left(\frac{2p}{\Lambda} \right)^3$$

one can arrive at the values of the azimuthal anchoring coefficient $W_a = 10^{-3} - 10^{-1}$ erg/cm^2, which is close to the values estimated in our experiments.

Note that the quality and perhaps even the type of alignment might be influenced by the specific divergence of plasma beam generated by ALT. The divergence characteristic of our source has been measured by Faraday cup. It shows that the majority of ions (>70%) is confined to the cone with the half angle of 3^0 at the top. In other words, the particle beam is well collimated. However, there is a part of ions divergent to quite big angles (>10^0). The 1st alignment mode can be affected by the central part of the beam. Since this part is well collimated, the direction of the induced easy axis depends on how the substrate is tilted with respect to the direction of the beam. The 2nd mode can be caused by ions strongly divergent in the direction perpendicular to the incidence plane of plasma beam.

4. Conclusions

We describe a procedure of plasma treatment of aligning substrates that yields different modes of alignment. The zero pretilt alignment is promising for bistable displays [12]. The procedure yielding non-zero pretilt alignment with a strong azimuthal anchoring may be used in LCD technologies, as it allows one to obtain a good quality of LC alignment at different plasma-etched organic and inorganic layers. The two-mode alignment opens new opportunities for patterning of the aligning substrates. The use of sheet like plasma fluxes generated by ALT allows to induce the described alignment on the large-scale substrates without translations.

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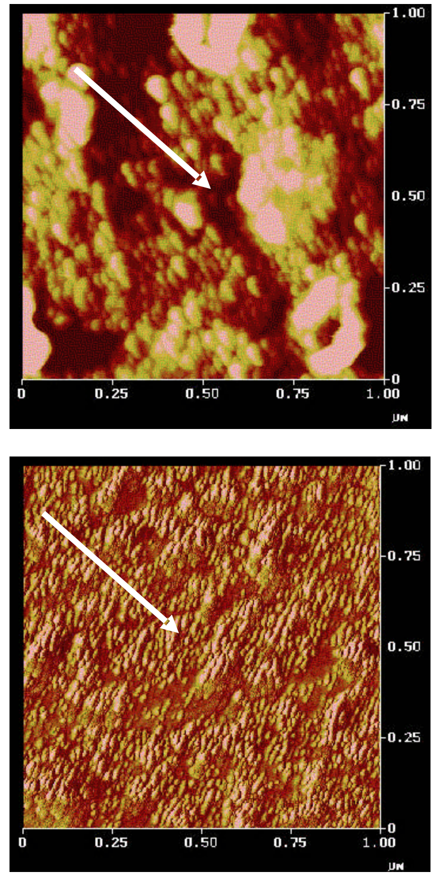

Figure 5. AFM images of the bare glass substrates irradiated at the conditions of the alignment mode 1 (a) and the alignment mode 2 (b). The arrow indicates projection of the plasma incidence direction onto the treated substrate.

6. References

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