

## Planar and Tilted Uniform Alignment of Liquid Crystals by Plasma Treated Substrates

O. Yaroshchuk<sup>1</sup>, R. Kravchuk<sup>1</sup>, A. Dobrovolsky<sup>1</sup>, L. Qiu<sup>2</sup>  
and O. D. Lavrentovich<sup>2,3</sup>

<sup>1</sup>Dept. of Crystals, Institute of Physics of NASU, pr. Nauki 46, 03028 Kiev, Ukraine e-mail:  
olegyar@iop.kiev.ua

<sup>2</sup>Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA e-mail: odl@lci.kent.edu

<sup>3</sup>Chemical Physics Interdisciplinary Program, Kent State University, Kent, OH 44242, USA

*We describe the new aligning technique that yields uniform planar or tilted orientation of a nematic liquid crystal at different organic and inorganic substrates. The method is based on the oblique irradiation of an aligning substrate with a partially collimated flux of accelerated plasma. The sheet-like plasma flux is produced by an anode layer thruster with a race track geometry of the discharge channel. For the liquid crystals with a positive dielectric anisotropy the technique produces two modes of uniform alignment: (1) with the easy axis in the incident plane of plasma beam; (2) with the easy axis perpendicular to the plane of incidence. The mode 1 transforms into the mode 2 when the irradiation dose increases. In mode 1, the pretilt angle can be controlled by changing the parameters of irradiation such as incidence angle, current density, particle energy, etc. In mode 2, the pretilt angle is zero (planar alignment). The azimuthal anchoring coefficient is relatively weak ( $W_a \sim 10^{-6}$  J/m<sup>2</sup>) for the first type of alignment and strong ( $W_a \geq 10^{-4}$  J/m<sup>2</sup>, comparable to the rubbed polymer substrates) for the second type. The two-mode alignment feature can be used to control the alignment properties and to create alignment patterns. The method is free of shortcomings known for the traditional rubbing technique. We discuss the possible mechanisms of the two-mode alignment and show that the plasma-induced modifications of the substrate topography might be an important factor in liquid crystal alignment.*

## I. Introduction.

Liquid crystal (LC) cells used in displays and other applications are usually uniformly aligned. There are three basic types of LC alignment. (1) Planar alignment with the LC director  $\mathbf{n}$  parallel to one axis in the plane of substrate. (2) Homeotropic alignment with  $\mathbf{n}$  perpendicular to the substrate. (3) Tilted LC alignment: the angle  $\theta$  between the substrate and the director (“pretilt angle”) is different from  $0^\circ$  and  $90^\circ$ . Many applications require tilted alignment with a small pretilt angle ( $\theta < 10^\circ$ ).

A uniform alignment of LCs is usually achieved by an appropriate treatment of the bounding substrates. The prevailing technique of planar/tilted alignment is unidirectional rubbing of thin polymer films deposited onto the substrates. However, this method often causes surface deterioration, generation of electrostatic charges and dust on the aligning surfaces. Besides, the rubbing technique is often hard to apply in the situations when a nontrivial alignment pattern is needed, as, for example, in the so-called multidomain alignment.

Recent years saw an increased interest to non-mechanical alignment techniques, such as photoalignment method [1,2], in which light irradiation causes surface anisotropy of the bounding plates. The method is relatively simple and yields highly uniform planar or tilted alignment. However, the corresponding strength of alignment, quantified by the so-called anchoring energy coefficient, is relatively weak; besides, some photoaligned substrates have 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 has been suggested [3].

Another approach to non-mechanical planar or tilted planar alignment is a treatment with oblique particle beams [4-11]. The particles might be ions, neutral particles, electrons and the mixtures thereof. With respect to the treatment effect, two types of particle beam alignment methods can be distinguished. In the first type, the beam is composed of the particles that serve as aligning material once deposited onto a bare substrate. The deposition might be direct (thermal deposition [4], etc.) or indirect (ion beam sputtering [5], etc.). In the second type of treatment, the particle beam is used to etch the aligning layer that was deposited prior to irradiation. For example, M.J. Little et al. [6] suggested oblique irradiation of the aligning films with the ion fluxes of high energy (1-3 keV). This method was further studied by Z.M. Sun et al. [7]. Recently, the IBM group modified this procedure by using flux of low energy ions (50-300 eV) [8-10]. 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 [8-10], the method provides excellent LC alignment on both organic and inorganic substrates.

Another example of particle beam is the plasma flux in which the charge of ions is compensated by electrons. Sprokel and Gibson [11] proposed to expose the bounding substrates to a “cold” r.f. plasma carried to the substrates with the directed gas stream; reaction of plasma and the substrate led to the structures capable of alignment. The plasma treatment through the

directed gas streams can be used in both etching and deposition regimes. It has been demonstrated that both regimes are capable of producing strong planar alignment.

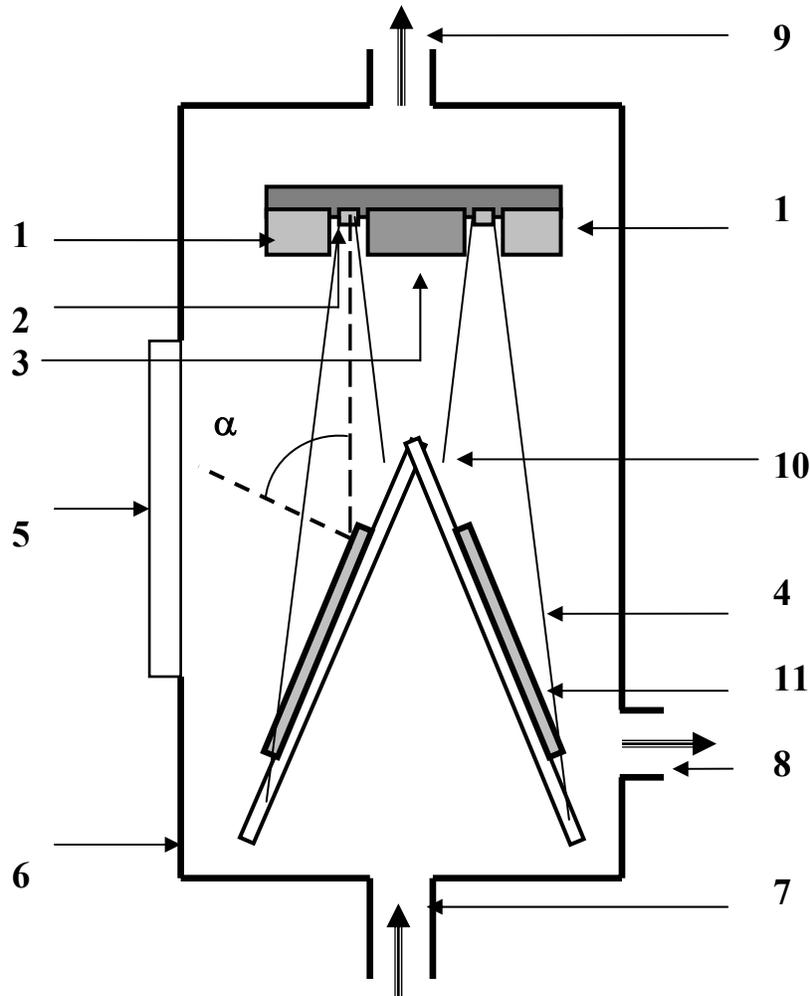
In the present work, we describe a different plasma alignment technique in which the aligning substrate is treated with a flux of plasma that is extracted and accelerated electrostatically. This plasma flux is generated with a reliable and simple d.c. plasma source known as the anode layer thruster (ALT). The discharge channel in the used ALT has the shape of a race track; the straight portions of this channel are used to produce the sheet-like fluxes. The ALT has been designed to generate collimated particle fluxes from practically any gaseous feed. Under certain operating parameters, with the inert gaseous feed, the proposed source yields the etching conditions similar to that described previously in Refs. [8-10]. An important difference, however, is that our technique produces **two** modes of planar LC alignment rather than one described in Refs. [8-10]. The two modes are both close to the planar alignment and represent (1) tilted planar (with a small pretilt  $\theta \leq 10^\circ$ ) and (2) strictly planar (zero tilt,  $\theta = 0$ ) alignment, with different geometrical (easy axis direction) and energetic (strength of anchoring) properties.

## II. Experimental.

### 1. *Ion source and Irradiation Procedure*

The ALT belongs to a family of closed drift thrusters (CDT) [12]. The CDT is the electro-dynamic thruster of high thrust efficiency. 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 are accelerated electro-dynamically, the grids to extract and accelerate ions are not needed too. Different types of CDTs are used on space satellites as ion rocket engines and in a variety of plasma etching and plasma deposition systems [12].

A scheme of ALT is shown in Fig. 1. The source has permanent magnets at the inner and outer cathodes. The anode is mounted in a space between the inner and outer cathodes. Together

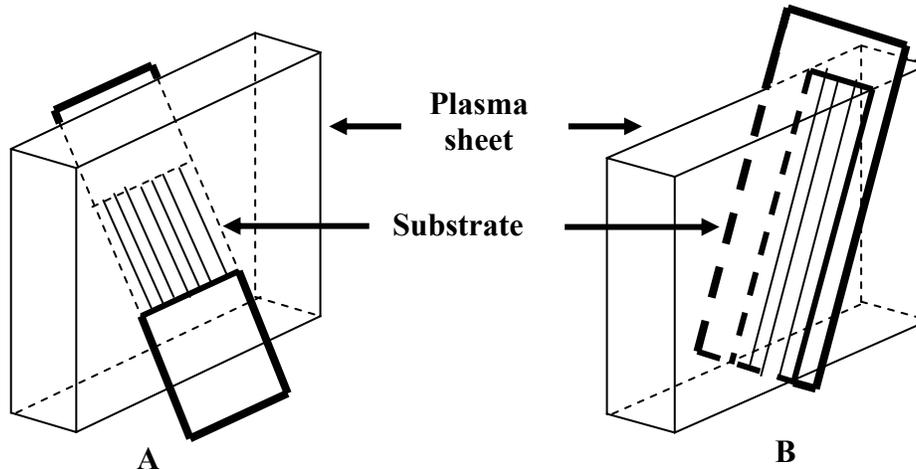


**Figure 1: Scheme of anode layer thruster and irradiation method. 1-outer cathode and N pole; 2 - anode; 3 - inner cathode and S pole; 4 - plasma flux; 5 – window; 6- body of vacuum chamber; 7, 8, and 9 – gas valves; 10 – substrate holder; 11 – substrate.**

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. In fact, it is a part of d.c. plasma generated in the discharge area. For more details, see Refs. [12,13].

The generated plasma flux has a shape of a hollow cylinder with a cross-section determined by the shape of the discharge channel. It might be circular or, as in the ALT we used, have a shape of the race track. The straight portions of the race track profile are suitable for a well-controlled treatment of large-area surfaces, provided the sample can be translated and tilted.

As the working gas for non-reactive treatment of the aligning substrates we used argon. The pressure  $P$  in the source chamber was  $(2-10) \cdot 10^{-4}$  Torr. It determined the current density  $j$  of  $\text{Ar}^+$  ions. The ion energy was controlled by the anode potential  $U$ . It was varied within the range 200-2000 eV\*. Therefore, the following three parameters of plasma irradiation were independently varied: 1) irradiation time  $\tau_{\text{exp}}$ ; 2) current density  $j$ ; 3) ion energy  $E$ .

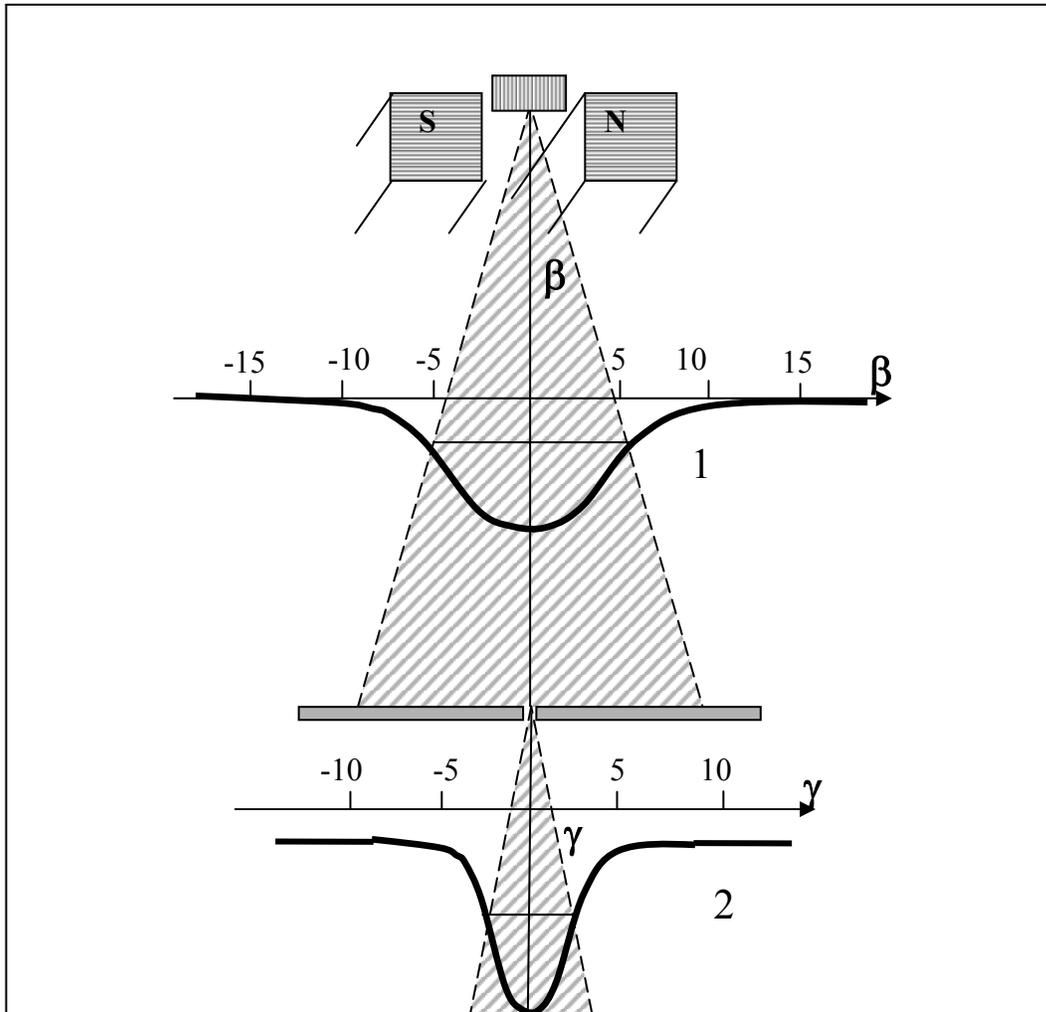


**Figure 2: Two different types of the sample orientation with respect to the plasma beam.**

The substrate holder was mounted in a vacuum chamber just under the discharge channel (Fig. 1). The approximate distance between the plasma outlet and the irradiated substrate was about 6 cm. The substrates of size of 30x20 mm were irradiated slantwise. We used two different sample settings with respect to the plasma sheet (Fig. 2). The plasma beam incidence angle  $\alpha$  was varied between  $0^\circ$  (normal to the substrate) and  $80^\circ$ ; see Fig. 1. To create alignment patterns, we used paper or plastic masks placed onto the treated substrates.

We characterized the beam intensity profile by scanning a probe across the beam. This distribution is of Gaussian shape (Fig. 3, curve 1). Half-width of the beam intensity distribution corresponds to the cone of the angle  $\beta \approx 6^\circ$  with the apex in the discharge area. The divergence of beam within this cone was further analysed 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

\* More precisely, the anode potential  $U$  determines the maximum energy of  $\text{Ar}^+$  ions. The energy spectrum of generated ions is broad with the maximum at approximately  $\frac{2}{3} e U$ . In the following we consider maximum ion energy, i.e.  $E=eU$ .



**Figure 3:** Scheme illustrating the beam profile (curve 1) and the beam divergence (curve 2).

mounted on the bottom of Faraday cup. This distribution is shown in Fig. 3, 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 ( $>10^\circ$ ).

## 2. Samples and Methods of the LC Alignment Characterization

We used a variety of organic polymers and inorganic coatings as aligning substrates for LC cells. Among them were polyimide PI 2555 purchased from Dupont, polyvinylcinnamate (PVCN) and polymethylmethacrylate (PMMA) from Aldrich. 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. As inorganic substrates, we mainly used bare glass slides (microscope slides purchased from Fisher Scientific) and ITO coated glass slides. We also

used a-C:H films obtained by plasma enhanced chemical vapor deposition (the preparation method was described earlier in Ref. [14]). The irradiation conditions were optimized for each type of substrates.

The LC alignment was studied by preparing two types of LC cells: (1) asymmetric cells in which one substrate was treated with the plasma beam, while the second substrate had a rubbed polyimide layer; and (2) symmetric cells, in which both bounding plates were irradiated with the plasma beam. To obtain a uniform director orientation, the cells were assembled in an antiparallel fashion, meaning that the directions of plasma beams treatment of the two opposite bounding plates were antiparallel to each other. The cell gap was kept by spacers of diameter 6  $\mu\text{m}$  and 15  $\mu\text{m}$ . The cells were filled with the nematic LCs pentylcyanobiphenyl (5CB) and ZLI4801-000 purchased from Merck.

The symmetric cells were used to measure the pretilt angle by crystal rotation method [15]. The asymmetric cells were prepared to determine the direction of LC alignment in the plane of the plasma treated substrate. Cells with twisted director were used to estimate the azimuthal anchoring coefficient as described in Refs. [16,17]. The azimuthal anchoring was also characterized by the method suggested in Ref. [18]. Besides the anchoring coefficient, this method [18] allowed us to elucidate the conditions of easy axis gliding and LC alignment memory. The polar anchoring was characterized by the “retardation vs. voltage” method [19].

### III. Results and Discussion.

#### 1. LC alignment

The uniform alignment in the LC cells with the plasma treated substrates is achieved for a wide range of irradiation parameters:  $j = (0.5-30) \mu\text{A}/\text{cm}^2$ ,  $E = (200-2000) \text{eV}$ ,  $\tau_{\text{exp}} = 0.1 - 20 \text{min}$ .

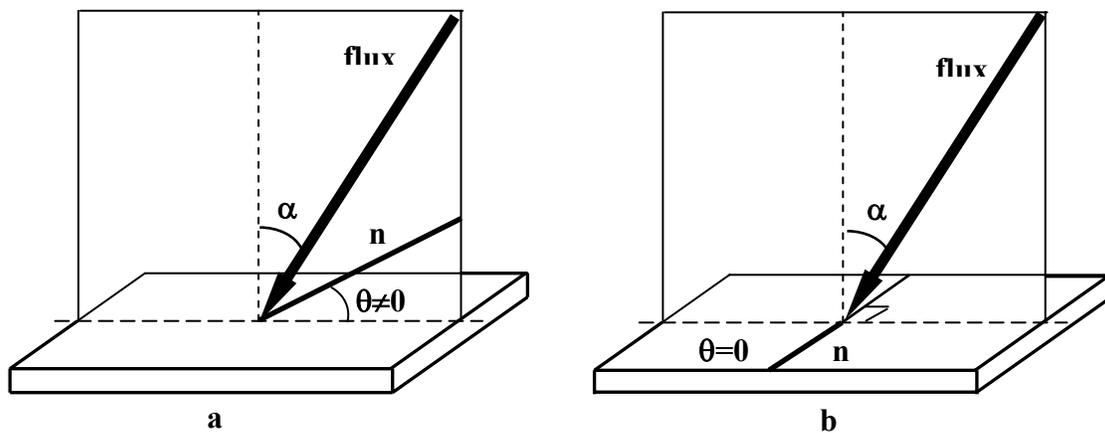


Figure 4: Irradiation geometry and LC alignment in the 1<sup>st</sup> (a) and the 2<sup>nd</sup> (b) modes.

These ranges overlap with the ones used by IBM group [8-10]. However, in contrast to the data reported in Refs. [8-10], we observe two different modes of LC alignment, Fig.4.

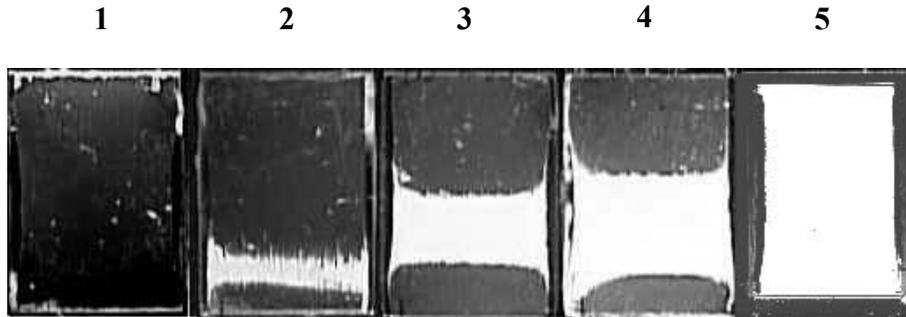


Figure 5: Photos of a set of asymmetric cells viewed between two crossed polarizers. One plate of the cells contains a rubbed PI layer and another plate contains a PVCN layer treated with plasma beam in geometry A, Fig. 2. The plasma irradiation parameters are  $\alpha=60^\circ$ ,  $E=600$  eV,  $\tau_{exp}=10$  min. The ion current density  $j$  is 1, 2, 5, 7, and  $9 \mu A/cm^2$  for the cells 1, 2, 3, 4, and 5, respectively. The cells are  $15 \mu m$  thick and filled with 5CB. The figure shows the alignment mode 1 in the cell 1, regions with the 1<sup>st</sup> mode and the 2<sup>nd</sup> alignment mode (dark and bright areas, respectively) in the cells 2, 3, and 4, and alignment mode 2 in the cell 5. Transition from dark to bright texture is caused by  $90^\circ$  reorientation of LC at the plasma treated substrate.

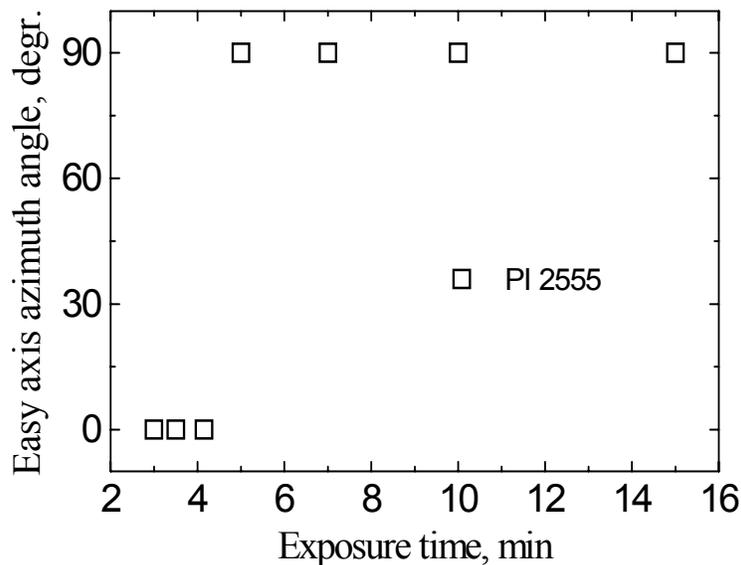
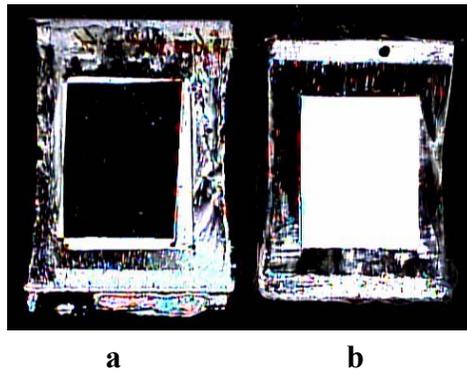


Figure 6: Azimuthal angle of the LC easy axis at plasma treated PI substrate as a function of irradiation time. The data are practically the same for 5CB and ZLI 4801-000 nematic LCs.

In the first mode, the easy axis of LC is in the incident plane formed by the direction of beam and the normal to substrate and tilts in the direction of the beam; the pretilt angle  $\theta$  is generally non-zero. In the second mode, the easy axis is perpendicular to the plane of incidence,  $\theta=0$ . Fig. 5 shows that the transition from the 1<sup>st</sup> mode to the 2<sup>nd</sup> mode is caused by the increase of current density of the argon ions. The 2<sup>nd</sup> mode appears initially in the area irradiated with the central, most intensive part of the beam, Fig.5. A similar alignment transition



**Figure 7: Photos of two asymmetric cells filled with 5CB viewed between two crossed polarizers. The cells contain rubbed PI substrate as the reference substrate and plasma treated glass slide as the object substrate. The object substrates were irradiated through the mask opening rectangular area in the middle of the substrate. The irradiation geometry and the cell assembling process are same for both cells. The irradiation dose corresponds to the mode 1 in the cell (a), and to the mode 2 in the cell (b). Dark state of the oriented part of the cell (a) implies that LC alignment on the plasma treated substrate is parallel to the alignment on the reference substrate. Analogously, bright state of the cell (b) means that LC alignment on the plasma treated substrate is perpendicular to the alignment on the reference substrate. Both cells demonstrate high quality of LC alignment.**

occurs when the irradiation time increases, Fig. 6. In other words, the type of alignment is controlled by the irradiation dose. A change of ion energy does not cause the transition from the 1<sup>st</sup> to the 2<sup>nd</sup> modes. The two-mode alignment is observed for both sample settings shown in Fig. 2 and for both nematic materials used in the experiments.

Note that both these materials have a positive dielectric anisotropy,  $\Delta\varepsilon > 0$ . The same two-mode alignment has been observed for other LCs with  $\Delta\varepsilon > 0$ . However, our preliminary data for the materials with  $\Delta\varepsilon < 0$  such as the mixture MJ961180 (Merck Korea) reveal only the 1<sup>st</sup> alignment mode with a high pretilt angle ( $\theta > 20^\circ$ ). The trend is similar to the behavior of the  $\Delta\varepsilon > 0$  and  $\Delta\varepsilon < 0$  LCs aligned by oblique deposition of  $\text{SiO}_x$  coatings [20,21]. In what follows, we refer to the materials with  $\Delta\varepsilon > 0$  only; the differences in the alignment of  $\Delta\varepsilon > 0$  and  $\Delta\varepsilon < 0$  LCs will be discussed elsewhere.

1.1 Alignment mode 1

A typical sample aligned in the 1<sup>st</sup> mode is shown in Fig. 7a. The pretilt angle is not zero and the LC easy axis is in the plane of incidence. The pretilt angle can be controlled in a

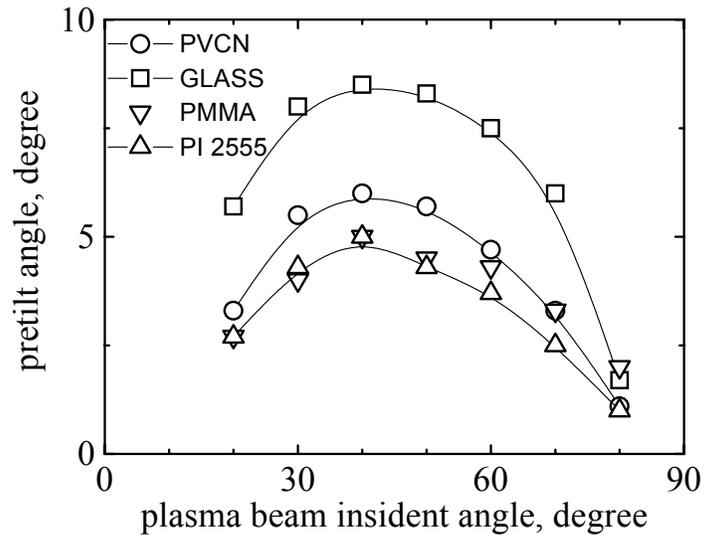


Figure 8: The pretilt angle  $\theta$  vs the plasma beam incidence angle  $\alpha$  for different substrates in 5CB cells. The irradiation parameters for polymer and glass substrates are  $j=8\mu\text{A}/\text{cm}^2$ ,  $E=600\text{ eV}$ ,  $\tau_{\text{exp}}=1.5\text{ min}$  and  $j=2\mu\text{A}/\text{cm}^2$ ,  $E=500\text{ eV}$ ,  $\tau_{\text{exp}}=1.5\text{ min}$  respectively. The cells gap is  $15\mu\text{m}$ .

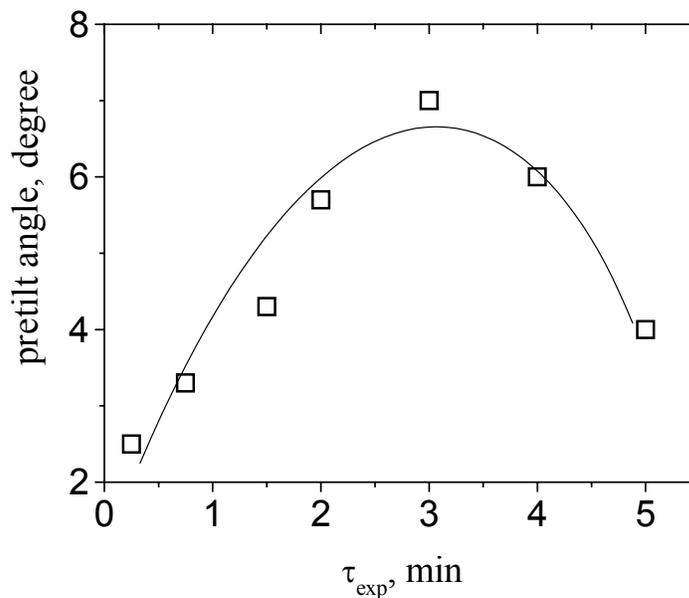
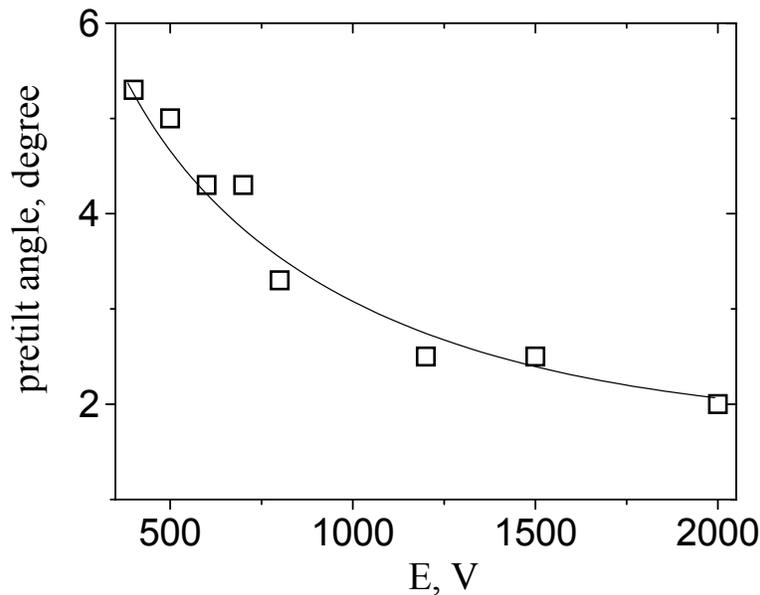


Figure 9: The pretilt angle vs irradiation time curve as measured for PI2555 substrate in the 5CB cell. The irradiation parameters are  $\alpha=50^\circ$ ,  $j=8\mu\text{A}/\text{cm}^2$ ,  $E=600\text{ eV}$ . The cells gap is  $15\mu\text{m}$ .

relatively broad range  $0^0 < \theta < 10^0$  by changing the irradiation parameters. Fig. 8 shows how  $\theta$  changes with the beam incidence angle  $\alpha$ . The functions  $\theta(\alpha)$  measured for different aligning films are non-monotonous with the maximum at  $\alpha=40^0-50^0$ . The variation of  $\theta$  with exposure time  $\tau_{exp}$  is presented in Fig. 9. This curve is also non-monotonous with a quasi-linear growth at small  $\tau_{exp}$ , saturation and rapid decrease in the vicinity of the transition to the 2<sup>nd</sup> mode. The pretilt angle monotonously decreases with the ion energy (anode potential), Fig. 10, which suggests that for an ion energy corresponding to the voltage less than 300 V, one might achieve a pretilt angle larger than  $10^0$ . However, we could not verify this possibility as the operation voltage threshold of our source was about 300 V.



**Figure 10.** The pretilt angle vs ion energy curve obtained for PI2555 substrate in the 5CB cell. The irradiation parameters are  $\alpha=50^0$ ,  $j=8 \mu\text{A}/\text{cm}^2$ ,  $\tau_{exp}=1.5 \text{ min}$ . The cells gap is  $15 \mu\text{m}$ .

The azimuthal anchoring energy coefficient  $W_a$  in the 1<sup>st</sup> alignment mode has been estimated to be of the order of  $10^{-6} \text{ J}/\text{m}^2$ . It is comparable to the values reported for the surface memory effect [22] and photo-alignment [23]. Thus the 1<sup>st</sup> mode of alignment is close to the alignment mode reported by the IBM group [8-10] with that exception that the azimuthal anchoring coefficient  $W_a$  in our case is relatively low. Some other aspects of LC alignment in the 1<sup>st</sup> mode, including combination of plasma treatment with phototreatment and rubbing, can be found in Refs. [24,25].

## 1.2 Alignment mode 2

A LC cell aligned in the 2<sup>nd</sup> mode is shown in Fig. 7b. The easy axis is perpendicular to the plane of incidence. The pretilt angle is zero,  $\theta = 0$ . The azimuthal anchoring corresponding to the 2<sup>nd</sup> mode is strong,  $W_a \geq 5 \times 10^{-4} \text{ J/m}^2$  (which is the limit of our measuring methods). No gliding of easy axis is observed. The polar anchoring coefficient is of the order of  $10^{-4} \text{ J/m}^2$ . The results are similar for the polymer aligning films (PI, PVCN, PMMA) and for bare glass and are comparable to those usually reported for the rubbed polymer aligning substrates. The LC alignment of the 2<sup>nd</sup> type has been previously described for some rubbing [26] and photoaligning processes [27]. The two-mode alignment was also observed for the obliquely deposited  $\text{SiO}_x$  films [20,21,28], but not for etching techniques.

Note that many applications require simultaneously a non-zero pretilt angle and a strong in-plane anchoring. ALT-generated plasma alignment can satisfy both these conditions, if one uses a procedure of subsequent steps of sample irradiation. For example, one can first align the substrate in the 2<sup>nd</sup> mode, then reorient the substrate by  $90^\circ$  and plasma-align it again according to the 1<sup>st</sup> mode to cause a non-zero pretilt angle  $\theta$ . As we verified experimentally, the resulting alignment is characterized by both strong anchoring ( $W_a \geq 10^{-4} \text{ J/m}^2$ ) and a non-zero pretilt angle ( $0^\circ < \theta < 5^\circ$ ).

## 1.3 Alignment stability

In order to check the thermal stability of LC alignment at the plasma treated substrates, the cells were exposed to a prolonged heating at  $90^\circ \text{ C}$  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 ( $15 \text{ mW/cm}^2$ , 1 hour).

The quality of LC alignment does not degrade with the sample aging at the room conditions. At the same time, such aging may cause the decrease of pretilt angle. The characteristic time of this process is about several weeks (Fig. 11). The pretilt angle aging can be explained by the appearance of low-molecular weight products of plasma etching at the substrate and their partial dissolution in the LC. As Fig. 11 illustrates, aging effects in some materials are less dramatic than in others. Therefore, one can mitigate the negative impact of aging by a proper material selection.

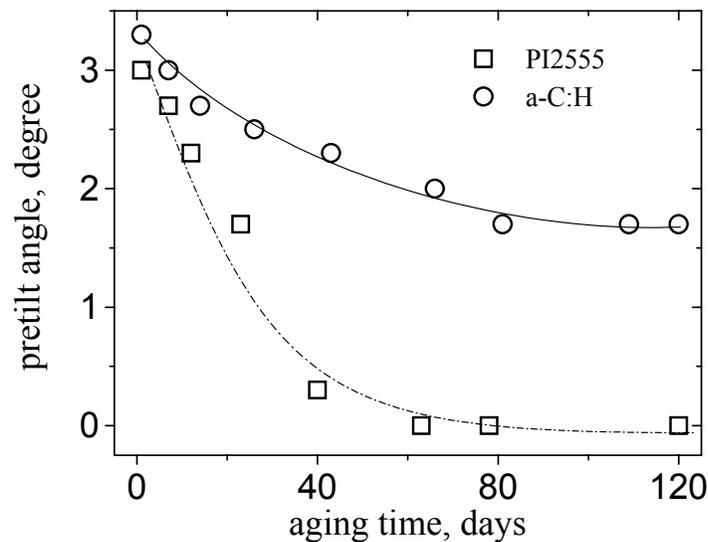


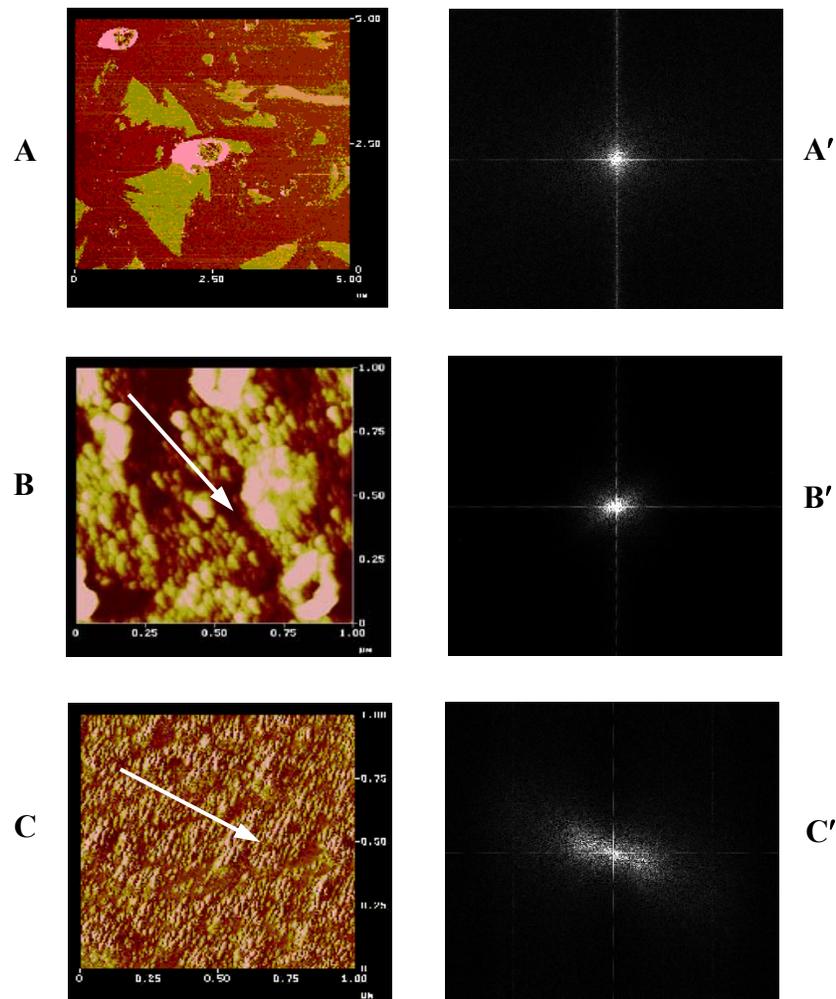
Figure 11: The pretilt angle vs cell aging time for the 5CB cells with PI2555 and a-C:H substrates. Room conditions.

## 2. LC alignment mechanisms

The nature of LC alignment depends on a number of factors. One of the most important is the direct anisotropic interaction between the molecules of two adjacent media. Another factor is topographical and relates 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 yields the smallest energy of elastic distortions.

Using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy sensitive to surface layers, Stöhr et al. [10] detected anisotropic distribution of the molecular groups at the surface of aligning films treated with an oblique ion beam. This anisotropy was explained by selective destruction of the molecular bonds by the ions. Qualitatively, a molecular group that is extended in the direction of the incident oblique beam is less likely to be destroyed than a molecular group that extends in the direction perpendicular to the beam.

Certainly, the mechanism of angularly-sensitive destruction of molecular bonds outlined above might play an important role in the aligning mechanism of the present technique. However, the topography of the substrates can also be important, as discussed below.



**Figure 12: AFM images of the untreated (A) and plasma treated glass substrates (B, C). The substrates B and C were treated for the 1<sup>st</sup> and the 2<sup>nd</sup> alignment mode, respectively. The arrow shows the direction of plasma beam. Parts A', B' and C' are Fourier transformations of the images A, B and C.**

We studied the surface profile of the plasma treated substrates by atomic force microscopy (AFM Nanoscope IIIa), Fig. 12. The plasma-treated surfaces become rougher as compared to untreated substrates, similarly to the results of other studies [29]. In our case, plasma treatment (in both modes) creates surface features of an average size 10-100 nm, elongated along some preferred directions. In the 1<sup>st</sup> mode, these features seem to be randomly distributed; they are elongated along the plane of incidence, Fig. 12, parts B and B'. In the 2<sup>nd</sup> mode a rough uneven ridge system develops and extends perpendicularly to the plane of incidence, Fig. 12, parts C and C'. As the system of ridges does not brake the symmetry with respect to the plane of incidence, no pretilt should be generated in the 2<sup>nd</sup> mode, as observed.

As demonstrated long time ago by Berreman for a substrate that favors in-plane orientation, the “groves” and “ridge” topography determines both the direction (usually along the grooves) and the strength of in-plane anchoring [30]. According to the Berreman model for sinusoidally modulated substrate [30], the azimuthal anchoring coefficient  $W_a$  is determined by the amplitude

$a$  and the wavelength  $\Lambda$  of the surface modulations,  $W_a = \frac{1}{2} K a^2 \left( \frac{2\pi}{\Lambda} \right)^3$ . With the typical  $a = 0.4$ -1 nm and  $\Lambda = 10 - 50$  nm and the Frank elastic constant  $K=10$  pN, one arrives at  $W_a \approx (10^{-6} - 10^{-4})$  J/m<sup>2</sup> which is within the range of experimental data. Therefore, surface topography might be as important as the selective chemical bond scission, similarly to the case of oblique deposition of SiO<sub>x</sub> [4,28]. Significant modification of the surface profile in the present case of plasma etching and in SiO<sub>x</sub> deposition might explain why the azimuthal anchoring is stronger than in the case of photo-alignment, which usually produces smooth surface profiles [31,32].

It is important to clarify which of the plasma components (UV light, electrons, ions, neutral atoms) plays the most significant role in LC alignment. To elucidate the role of UV light, the photosensitive PVCN film was irradiated with a plasma beam through a quartz plate that is transparent for deep UV irradiation. UV/Vis spectrum of the film exhibited changes confirming UV light action. However, this UV irradiation did not result in LC alignment. This fact as well as the fact of LC alignment at the plasma treated non-photosensitive substrates (glass and ITO) show that the UV component may play only a secondary role in LC plasma-induced alignment. To test a hypothesis that the LC alignment might be caused by the electron component in the ALT flux, we used an indirect experiment, by treating the substrates with a sheet like e-beam generated by the electron beam machine CB150 from Energy Sciences Inc. (USA). The operation voltage and the current density were 175 keV and 180  $\mu$ A/cm<sup>2</sup>, respectively. During irradiation the samples were positioned obliquely to e-beam ( $30^\circ < \alpha < 70^\circ$ ) and moved with the velocity 0.19 m/s. These conditions correspond to irradiation dose about 100 kGy. The e-beam treated substrates show no aligning capabilities when used in LC cells. The results above, although very preliminary, indicate that the main mechanism of alignment by ALT-generated plasma fluxes involves primarily ions and, perhaps, neutral atoms that might be also present (in a much smaller quantities) in the plasma flux.

Let us discuss now the possible mechanisms of the two-mode alignment. As mentioned above, the similar multi-mode alignment regimes have been already described for alignment by rubbed polymer films [26], by photoalignment [27] and by SiO<sub>x</sub> deposition [28]. In the most popular rubbing technique, the director usually aligns along the direction of rubbing. However, a perpendicular mode of alignment, similar to the aligning mode 2 described above, is also known, as reviewed in a great detail recently [24]. Lee et al. [26] demonstrated that at least in the case of rubbed polystyrene films, rubbing might cause “grooves” perpendicular to the rubbing direction. Physically, such topography is natural, as many elastic bodies and films develop wrinkles perpendicular to the shear direction (the simplest experiment can be performed by rubbing a skin with a finger).

In photoalignment technique, in which the topography changes little, the easy axis is determined by orientational distribution of photosensitive fragments and their photoproducts. If there are different types of fragments with different aligning tendencies, one might observe several alignment modes [25].

In SiO<sub>x</sub> deposition [4,5,28], relatively small deposition angles ( $40^\circ < \alpha < 70^\circ$ ) cause the easy axis perpendicular to the plane of incidence of particle beam. For grazing deposition ( $\alpha \geq 80^\circ$ ), the easy axis is in the plane of incidence with a tilt toward the evaporation direction. This alignment transition is explained by the experimentally detected change in the anisotropy direction of the surface profile. Tilted deposition results in formation of elongated elevations

(needles, columns) tilted in the plane of deposition. Their growth results in merging of the individual needles into rows and also in a “self-shadowing” effect, considered by Smith [33]. The deposited grains prevent the new particles from reaching the substrate in the shadow of the grain. Consequently, vacant regions are left in the film and individual grains of material eventually join into a two-dimensional ridge structure with the long axis perpendicular to the plane of incidence. The study of surface topography suggests that the growing needles indeed form the rows elongated predominantly perpendicularly to the plane of incidence. Depending on the ratio of the width of the needle (and row) to the average repeat distance between the rows along the direction of deposition, the orientation might be of either first or second type. Usually, with  $40^\circ < \alpha < 70^\circ$  the alignment is perpendicular to the deposition plane; the reason is that the repeat distance is relatively small and director orientations other than perpendicular to the plane of incidence would lead to strong elastic distortions. In contrast, with grazing deposition, the rows of needles are far apart from each other and the LC can be aligned parallel to the plane of incidence.

The topographic features observed in plasma etching technique are somewhat similar to those detected for the films obtained by deposition. The different modes of alignment might be caused by the effect similar to the self-shadowing effect above, as the etched portions of the substrate with the slope along the direction of beam are less exposed to the flux.

Apart from this “shadow” effect, the topography changes observed in the AFM studies and manifested in the transformation of the 1<sup>st</sup> mode into the 2<sup>nd</sup> mode, might be also related to other mechanisms, in particular, to the finite divergence of the ALT plasma beam. The 2<sup>nd</sup> 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 second mode of alignment was never described for the substrates treated obliquely with the ion beams generated by the Kaufman plasma source [8-10,34-37]. Most likely, the irradiation parameters in the cited experiments were in the region of values where the topography does not change enough to cause the 2<sup>nd</sup> mode. Clearly, further studies are needed to elucidate the mechanisms in details.

### 3. *Practical value*

Let us compare the technique to other plasma methods that include deposition of various films [38-40] and post-deposition treatments, mainly by bombardment with reactive ions [41-43]. All these methods are capable of producing various values of zenithal anchoring coefficient and pretilt angle but not a uniform planar alignment; mostly because the substrates are placed in the gas discharge area where the plasma treatment is practically isotropic. Sprokel et al. [11] proposed a *directed* plasma flux and anisotropic treatment, which resulted in a uniform planar alignment. This was achieved by the use of a modified r.f. plasma etcher in which reactive plasma was extracted and carried onto substrates by the gas stream. In our experiments, plasma is extracted and accelerated electrostatically to relatively low energies that treat only a thin layer of the substrate, similarly to the procedure described for ion beams [8-10]. Thus the ALT source allows one to combine the advantageous anisotropic treatment with collimated plasma fluxes and the optimized energies of ions. Note that the ALT source can be scaled up to treat substrates of large size (meters). Reliability, simplicity of construction, high thrust efficiency and easiness of treatment of substrates make this source attractive for technological applications.

One of the main advantages of the described procedure is that it yields several regimes of LC alignment, namely:

- 1) First mode. Planar alignment with a weak azimuthal anchoring ( $W_a=10^{-6}$ - $10^{-5}$  J/m<sup>2</sup>) and relatively high pretilt angle  $\theta=(5^0$ - $10^0)$ .
- 2) Second mode: Planar alignment with strong anchoring ( $W_a>10^{-4}$  J/m<sup>2</sup>) and zero pretilt angle.
- 3) Subsequent treatment using the combinations of the basic two modes above: Planar alignment with strong anchoring ( $W_a>10^{-4}$  J/m<sup>2</sup>) and moderate pretilt angle  $\theta=(0^0$ - $5^0)$ .

Each of these regimes is attractive for modern LCD technologies. The first alignment regime may be useful for LCD based on the easy axis gliding [44]. The second regime is promising for bistable nematic displays [45]. Finally, the third regime may replace standard rubbing procedure widely used in modern LCD technology.

The two-mode alignment opens new opportunities for the patterning of LC alignment. For instance, the two-domain azimuthal patterning can be realized by only one masking step without any rotation of the substrate. The processing scheme and the photographs of the sample aligned in this manner are presented in Fig. 13. Evidently, all patterning procedures described for other etching alignment methods are feasible for our case, too. Moreover, for sample patterning, the plasma alignment method may be combined with other methods of LC alignment.

The electro-optic properties of the cells aligned by plasma treatment are very similar for those of the cells prepared with rubbing method [25]. We observed no substantial differences in dielectric constants  $\epsilon'$  and  $\epsilon''$ , and in their frequency dependencies, for LC cells prepared by these two methods.

Finally, it is worth mentioning that the proposed aligning procedure is compatible with other vacuum processes employed in LCD industry (ITO deposition, TFT coating, vacuum filling of LCD, etc.). One might expect that an entirely vacuum technological line of LCD production can strongly reduce the well-known problems related to dust, humidity, air ions etc.

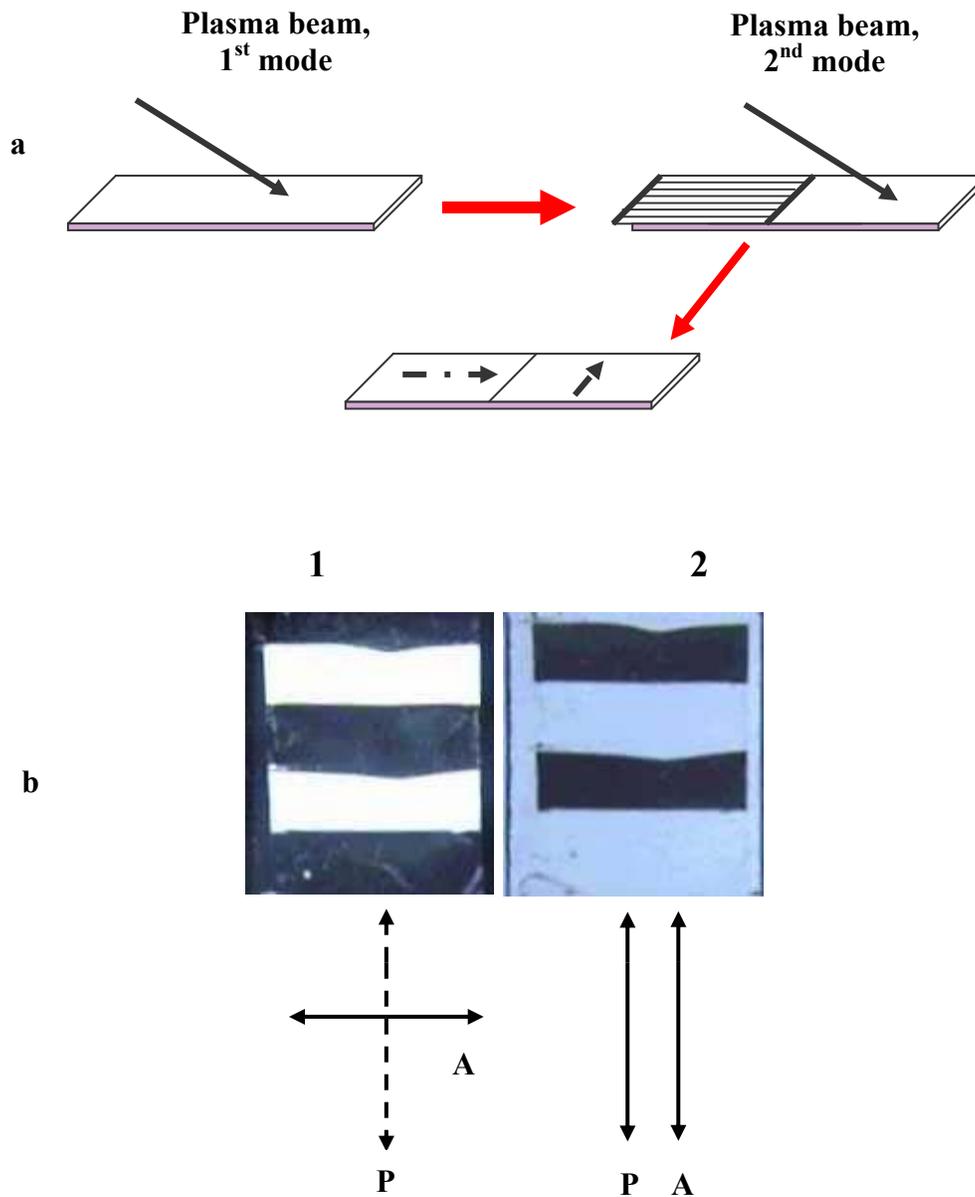


Figure 13. The patterning scheme based on alignment transition 1<sup>st</sup> mode-2<sup>nd</sup> mode (a) and the photographs of a LC cell viewed between a pair of crossed and parallel polarizers (b). The cell is asymmetric with one rubbed PI substrate and one plasma treated PI substrate. To obtain the pattern, the whole area of the latter substrate is first irradiated with the plasma beam ( $E=600V$ ,  $j=7 \mu A/cm^2$ ,  $\alpha=60^0$ ) for  $\tau_{exp} = 2.5$  min; then the portions of the substrate are covered with the mask and the remaining regions are exposed to the same plasma beam for additional  $\tau_{exp} = 10$  min. The dark and bright areas of the texture correspond to two different LC orientations at the plasma treated substrate: parallel and perpendicular to the alignment direction on the PI substrate, respectively.

#### **IV. Conclusion.**

We have presented the new ion/plasma aligning technique that yields two basic modes of uniform LC alignment on the variety of organic and inorganic substrates: (1) tilted with the director in the plane of incidence and (2) planar with the director perpendicular to the plane of incidence and thus zero pretilt. The plasma treatment results in anisotropic modification of the aligning substrates; different modes of alignment are related to different topographical features of the treated substrates. In particular, in the second mode, one observes series of ridges developing at the treated substrate in the direction perpendicular to the plane of incidence.

The alignment in both modes is of high quality with a good thermal and photo stability. The technique allows one to control the pretilt angle and to obtain a high in-plane (azimuthal) anchoring coefficient. The two-mode alignment opens new opportunities for patterning of the aligning substrates.

#### **Acknowledgements**

We thank I. Dozov and P. Martinot-Lagarde (Nemoptic, France), L.-C. Chien (Liquid Crystal Institute, USA) for fruitful discussions. We also greatly acknowledge support of I. Dozov in anchoring studies and U. Maschke (University of Lille, France) in e-beam irradiations.

## V. References.

1. A. Dyadyusha, V. Kozenkov, T. Marusii, Yu. Reznikov, V. Reshetnyak, and A. Khizhnyak. "Light-induced planar alignment of nematic liquid crystal on anisotropic surface without microgrooves", *Ukr.Phys.J.*, **36**, 1059-1061 (1991).
2. M. Schadt, K. Schmidt, V. Kozinkov, and V. Chigrinov, "Surface-Induced Parallel Alignment of Liquid Crystals by Linearly Polymerised Photopolymers", *Jpn.J.Appl.Phys.*, **31**(7), Part 1, 2155 -2164 (1992).
3. M. Hasegawa, "Key Molecular Structure Determination of Photoalignment Materials from the Effects of Linearly Polarized Deep UV Light on Several Polymers", *Jpn.J.Appl.Phys.*, **39**(3A), Part 1, 1272-1277 (2000).
4. J. Janning, "Thin film surface orientation for liquid crystals", *Appl.Phys.Lett.*, **21**(4), 173-174 (1972).
5. T. Motohiro and Y. Taga, "Sputter-deposited SiO<sub>x</sub> films for liquid crystal alignment", *Thin Solid Films*, **185**, 137-144 (1990).
6. M.J. Little et al., "Means and method for inducing uniform paralel alignment of liquid crystal material in a liquid crysatl cell." US Patent No 4,153,529 (1979).
7. Z.M. Sun, J.M. Engels, I. Dozov, and G. Durand, "Ar<sup>+</sup> beam sputtering on solid surfaces and nematic liquid crystal orientation", *J. Phys. II France*, **4**, 59-73 (1994).
8. P. Chaudhari, J. Lacey, S.A. Lien, and J. Speidell, "Atomic Beam Alignment of Liquid Crystal", *Jpn. J. Appl.Phys.*, **37**,(1-2), L55-L56 (1998).
9. P. Chaudhari et al., "Atomic-beam alignment of inorganic materials for liquid-crystal displays", *Nature*, **411**, 56-59 (2001).
10. J. Stöhr, M.G. Samant, J. Lüning, A.C. Callegari, P. Chaudhari, J.P. Doyle, J.A. Lasey, S.A. Lien, S. Purushothanam, and J.L. Speidell, "Liquid Crystal Alignment on Carbonaceous Surfaces with Orientational Order", *Science*, **292**, 2299-2302 (2001).
11. G.J. Sprokel and R.M. Gibson, "Liquid Crystal Alignment Produced by RF Plasma Deposited Films.", *J.Electrochem.Soc.*, **124**(4), 559-561 (1977).
12. V. Zhurin, H. Kaufman, and R. Robinson, "Physics of closed drift thrusters", *Plasma Sources Sci. Technol.*, **8**, R1-R20 (1999).
13. J.E. Keem, *Proc. of 44<sup>th</sup> Annual Techn. Conference of SVC*, 1 (2001).
14. O. Yaroshchuk, R. Kravchuk, A. Dobrovolsky, N. Klyui, and O. Korneta, "LC alignment on the inorganic substrates treated with directed plasma flux." *Proceed. of XI<sup>th</sup> Intern. Symposium "Advanced Display Technologies"*, Crimea, Ukraine., 186-194 (Sept. 8-12, 2002)
15. G. Baur, V. Wittwer, and D. W. Berreman, "Determination of the tilt angles at surfaces of substrates in liquid crystal cells", *Phys. Lett. A*, **56**, 142-144 (1976).
16. A. Rapini and M. Papoular, *J.Phys. Colloq. (France)*, **30**, C4-54 (1969).

17. G. Bryan-Brown and I. Sage, "Photoinduced ordering and alignment properties of polyvinylcinnamates", *Liquid Crystals*, **20**(6), 825-829 (1996).
18. E. Polossat and I. Dozov, "New optical method for the measurement azimuthal anchoring energy of the nematic liquid crystals", *MCLC*, **282**, 223-233 (1996).
19. Yu. A. Nastishin, R. Polak, S.V. Shiyankovskii, V. Bodnar, and O. D. Lavrentovich, "Nematic polar anchoring strength measured by electric field techniques", *J.Appl. Phys.*, **86**, 4199-4213 (1999).
20. M. Lu, K.H. Yang, and J.S. Chey, "Homeotropic Alignment of Liquid Crystals by Single Evaporation of SiO<sub>2</sub>", *IDW'99*, 121-124 (1999).
21. M. Lu, K.H. Yang, T. Nakasugi, and J.S. Chey, "Homeotropic Alignment of Liquid Crystals by Single Evaporation of SiO<sub>2</sub> and Its Application to High Resolution Microdisplays", *SID 00 Digest*, 446-449 (2000).
22. R. Barberi, I. Dozov, M. Giocondo, M. Iovane, Ph. Martinot-Lagarde, D. Stoenescu, S. Topchev, and L. Tsonev, "Azimuthal anchoring of nematic on undulated substrate: Elasticity versus memory", *Eur.Phys.J.*, **B6**, 83-91 (1998).
23. M. O'Neill and S.M. Kelly, "Photoinduced surface alignment for liquid crystal displays", *J.Phys.D: Appl.Phys.*, **33** R67-R84, (2000).
24. O. Yaroshchuk, Yu. Zakrevskyy, A. Dobrovolskyy, S. Pavlov, "Liquid crystal alignment on the polymer substrates irradiated by plasma beam", *Proc. SPIE*, **4418**, 49-53 (2001).
25. O. Yaroshchuk, R. Kravchuk, A. Dobrovolskyy, S. Pavlov, "Plasma treatment as a method of in-plane LC alignment", *Proc. Eurodisplay'02*, 421-424 (2002).
26. S.W. Lee, B. Chae, H.C. Kim, B. Lee, W. Choi, S.B. Kim, T. Chang, and M. Ree, "New Clues to the Factors Governing the Perpendicular Alignment of Liquid Crystals on Rubbed Polystyrene Film Surfaces", *Langmuir* **19**, 8735 -8743 (2003).
27. Yu. Reznikov, O. Yaroshchuk, I. Gerus, A. Homuth, G. Pelzl, W. Weissflog, K.J. Kim, Y.S. Choi, and S.B. Kwon, "Relationship between molecular structure of photosensitive fragments and aligning properties of polysiloxanes", *Mol.Materials*, **9**, 333-342 (1998).
28. W. Urbach, M. Boix, and E. Guyon, "Alignment of nematics and smectics on evaporated films", *Appl.Phys.Lett.*, **25**(9), 479-481 (1974).
29. O.D. Greenwood, J. Hopkins, and J.P.S. Badyal, "Non-isothermal O<sub>2</sub> Plasma Treatment of Phenyl-Containing Polymers", *Macromolecules*, **30**, 1091-1098 (1997).
30. D.W. Berreman, "Solid Surface Shape and the Alignment of an Adjacent Nematic Liquid Crystal", *Phys.Rev.Lett.*, **28**, 1683-1686 (1972).
31. B. Cull, Y. Shi, S. Kumar, and M. Schadt, "Anisotropic surface morphology of poly(vinyl 4-methoxy-cinnamate) and 12-8(poly)diacetylene thin films induced by linear photopolymerization", *Phys. Rev. E*, **53**(4), 3777-3781 (1996).
32. P.O. Jackson, G. Bergmann, J.H.C. Hogg, M.O'Neill, P. Hindmarsh, S.M. Kelly, and G.F. Clark, "Grazing incidence X-ray reflectivity of coumarin side-chain polymers used for liquid crystal photoalignment layers", *Synthetic Metals*, **127**, 95-98 (2002).
33. D.O. Smith, M.S. Cohen, G.P. Weiss, *J.Appl.Phys.*, **31**, 1755 (1960).
34. Y. Kato et al., "Hydrogenated Amorphous Carbon Film Used as an Alignment Layer for Liquid Crystal Displays", *Eurodisplay 02*, 525-529 (2002).

35. J.Y. Hwang, Y.M. Jo, D.S. Seo, S.J. Rho, D.K. Lee, and H.K. Baik, "Liquid Crystal Alignment Capabilities on a New Diamond-Like Carbon Thin Film Layer", *Jpn.J.Appl.Phys.*, **41**, L654-L656 (2002).
36. J. West, L. Su, K. Artyushkova, J. Farrar, J. Fulghum, Y. Reznikov, "Study of Ion Beam Alignment of Liquid Crystals on Polymer Substrates", *SID 02 Digest*, 1102-1105 (2002).
37. K.H. Yang, G.T. Liang, S. Tanaka, and H. Endoh, "Ion-Beam Irradiated Thin Films for the Alignment of IPS LCD", *IDMC'03 Proceed.*, (2003).
38. J.C. Dubois, M. Gazard, and A. Zann, "Plasma-polymerized films as orientating layers for liquid crystals", *Appl.Phys.Letters*, **24**(7), 297-298 (1974).
39. R. Watanabe, T. Nakano, T. Satoh, H. Hatoh, and Y. Ohki, "Plasma-Polymerized Films as Orientating Layers for Liquid Crystals", *Jpn.J.Appl.Phys.*, **26**(3), 373-376 (1987).
40. A.I. Vangonen, and E.A. Konshina. "ATR-IR Spectroscopy Study of NLC Orientation at the Plasma-Polymerized Layers Surface", *Mol.Cryst.Liq.Cryst.*, **304**, 507-512 (1997).
41. N. Shahidzadeh, A. Merdas, and W. Urbach, "Orientation of Lyotropic and Thermotropic Liquid Crystals on Plasma-Treated Fluorinated Surfaces", *Langmuir*, **14**, 6594-6598 (1998).
42. J.G. Fonseca, P. Charue, and Y. Galerne, "Zenithal Anchoring Angle and Anchoring Strength on Oxidized Silane Plates", *Mol.Cryst.Liq.Cryst.*, **329**, 597-604 (1999).
43. S.P. Kurchatkin, N.A. Muravyeva, A.L. Mamaev, V.P. Sevostyanov, and E.I. Smirnova, "The method of the creation of aligning layer for liquid crystal display", Patent of Russia No 2,055,384.
44. Yu. Kurioz, V. Reshetnyak, and Yu. Reznikov, "Orientation of a Liquid Crystal on a Soft Photoaligning Surface", *Mol.Cryst.Liq.Cryst.*, **375**, 535 - 541 (2002).
45. I. Dozov, M. Nobili, and G. Durand, "Fast bistable nematic display using monostable surface switching", *Appl.Phys.Lett.*, **70**, 1179-1181(1997).