P-14: Plasma Treatment as a Method of In-Plane Liquid Crystal Alignment

Oleg Yaroshchuk*, Ruslan Kravchuk, Andriy Dobrovolskyy, and Sergiy Pavlov

Institute of Physics, NASci. of Ukraine, Prospect Nauki 46, 03028 Kyiv, Ukraine

Abstract

The high quality planar alignment of LC is obtained on a number of organic and non-organic substrates subjected to plasma irradiation. In contrast to the known methods of treatment in isotropic plasma used to modify zenithal anchoring and pretilt angle, new method operates with collimated plasma beams directed obliquely to the aligning substrates. In the range of irradiation parameters we used, the easy axis of LC alignment on all substrates is parallel to plasma propagation direction. Dependencies of the LC pretilt angle and anchoring energy on the incidence angle of the plasma beam, time of irradiation, energy and current density of the irradiation are investigated. The azimuth anchoring energy on the plasma treated substrates is close to that obtained by photoalignment method, whereas the pretilt angle is comparable with that generated by rubbing. The transmittance vs voltage curves are very similar for plasma and rubbing processes. Same as rubbing alignment, plasma induced alignment is highly thermally and photo-stable. The combined treatments plasma/polarized UV light and plasma/rubbing are considered as methods of LC patterning.

1. Introduction

The practice of the last years shows that rubbing method of liquid crystal (LC) alignment often hinders the further improvement of LCD. Among the methods alternative for rubbing, photoalignment is being most intensively studied [1]. Using this method, substrates are covered by photosensitive materials and subsequently irradiated with polarized light. Since mechanical contact with aligning substrate is avoided, this method is free from many drawbacks of rubbing technique, like surface deterioration or static electricity.

At the same time, the application of photoalignment method is restrained with several principle drawbacks compared with the widely spread rubbing method. These drawbacks are not sufficient thermal stability of the induced alignment, low azimuth anchoring energy, double degeneracy of the LC pretilt angle and its non-uniformity over the probe. In addition, LC alignment on the photoirradiated substrates is characterized by the pronounce image sticking effect which is a residual image when the controlling voltage is changed [2].

One or several of these disadvantages are characteristic for the known photoaligning materials. This gives the reason to conclude that shortcomings of photoalignment are mainly caused not by material properties, but treatment procedure. To our belief, Vis/UV light acts very softly on the aligning substrates. As result, the substrates are not capable to provide strong anchoring. The conclusion suggests that the irradiation treatment should be strengthened.

In the development of photoalignment, M. Hazegava [3] suggested to use deep UV irradiation. In this case, the photoalignment effect was observed for traditionally non-photosensitive polymers. One more radical solution suggested Chaudhari et.al. [4-6]. It consists in oblique irradiation of the aligning polymer substrates with a collimated ion beam. This method provides excellent LC alignment on both organic and non-organic substrates. Several modifications of this method are suggested. In [7] strong electric field is applied in the area close to the aligning substrate to redirect ions obliquely to the substrate. The other modification is proposed in [8] where ion beam irradiation is used in combination with rubbing as a method of cell patterning.

The advantages of deep UV irradiation and ion irradiation can be combined by the treatment of the aligning substrates with various kinds of plasma. The processing of the LC substrates with a glow discharge was earlier applied for surface etching, grafting of the aligning surfaces with O and F containing groups [9-11], as well as for plasma polymerization [12,13]. These processes allowed to vary zenital anchoring energy and pretilt angle of LC alignment. At the same time, generation of azimuthal alignment was not achieved. To provide planar LC alignment the aligning substrates were preliminarily rubbed using conventional procedure.

Common feature of the previous experiments was the use of isotropic plasma. Our approach first suggested in [14] is a use of *collimated* plasma beams to generate azimuth LC alignment. In the present paper, the potency of this method is shown on example of a number of organic and non-organic coatings.

2. Experimental

2.1. Substrates

As aligning materials we used photosensitive and non-photosensitive polymers as well. To the first series belonged polyvinylcinnamate (PVCN) from Aldrich and polyimide (PI) 2555 from Dupont, which are well-known photoaligning materials. Polymethylmethacrylate (PMMA) and polysulfone (PS) from Aldrich were used as non-photosensitive aligning polymer. The polymers were dissolved in a proper solvent and spin coated on the glass slabs containing ITO electrodes. In the following, the substrates were baked at the elevated temperature depending on the polymer coating and subjected to plasma irradiation. The film thickness of the polymer coatings estimated by profilometer was about several hundreds of nm. Also, bare glass slides (microscope slides from Fisher Scientific) and ITO coated glass slides were used for the plasma induced LC alignment.

2.2. Plasma Source and Irradiation

To irradiate probes we used anode layer ion source from the class of electrodynamic trusters [15]. This source is specially designed to produce a collimated flux of ions from practically any gaseous feed. The sketch of the anode layer truster is shown in Fig.1. The source contains permanent magnets on the inner and outer cathodes C. The anode A is above the inner and outer cathodes. Together these electrodes define the size and the shape of the discharge

* Corresponding author: olegyar@iop.kiev.ua

channel. The ion flux is formed in crossed **E** and **H** fields immediately within the discharge channel and so it is a part of d.c. plasma generated in the discharge area. In fact, the ion layer truster is a plasma source. This is a principle difference between the anode layer truster and the electrostatic ion truster of Kaufman type

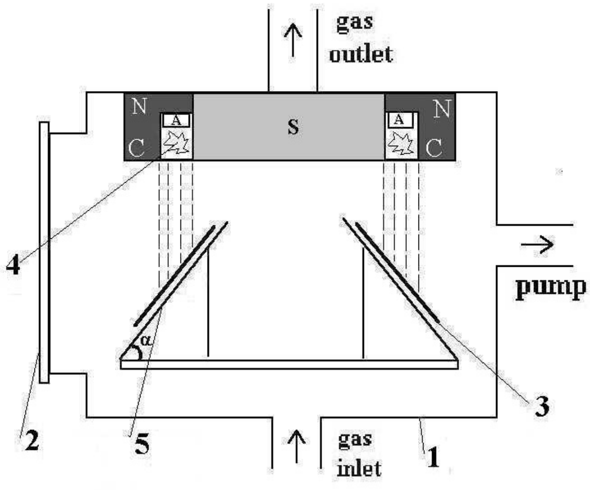

Figure 1. Schematic diagram of anode truster source and plasma irradiation set up. 1-body of vacuum chamber; 2-window; 3, 5-substrate holder; 4-discharge channel.

employed in [4-6]. Since plasma contains several active components (ions, neutral atoms, electrons and deep UV) one can expect qualitatively new aligning effects by the use of plasma treated substrates. The sheet like plasma fluxes produced by the anode layer sources allows to treat easily large-scale substrates (using translation method). Finally, the anode layer trusters have simplified construction. In contrast to electrostatic trusters, they do not require filaments or secondary electron sources to initiate discharge current or to neutralize the beam. In addition, since ions are accelerated electrodynamically, the anode layer trusters do not need grids to extract and accelerate ions.

In our set up the anode layer truster with the race track shape of the discharge channel is mounted in a vacuum chamber as shown in Fig.1. The chamber is pumped out up to pressure 10^{-5} Torr, and then is filled by argon. The working pressure *p* in our experiments was (2-10) 10^{-4} Torr. The pressure of Ar determined current density *j* of the plasma ions. The ion energy was determined by anode potential U. It was varied within 200-900 eV.

The substrate holder was mounted in a vacuum chamber just under the discharge channel (Fig. 1). A distance between plasma outlet and irradiated substrate was about 20 cm. To generate azimuthal alignment of LC, the substrates where irradiated slantwise. The plasma beam incidence angle α was varied within 20^0 and 80^0. To irradiate only part of the aligning substrate the masks made from aluminium foil or paper have been used.

In our experiments three parameters of plasma irradiation were varied: 1) irradiation time τ_{exp}; 2) current density *j*; 3) particle energy *E*.

A 250 W mercury lamp was used for UV irradiation. To generate a pretilt angle for the LC, the substrates were irradiated obliquely (with the angle between the substrate and beam direction at 45^0) in two steps; with polarized light (6 mW, 10 min) and then with non-polarized light (15 mW, 0.5 min). A Glan prism was used to polarize the UV light.

2.3. LC Cells and Its Characterization

Two kinds of LC cells were prepared: 1) one substrate is irradiated by plasma beam, while the second one is a rubbed polyimide layer (combined cells); and 2) with both substrates irradiated by plasma beam (symmetrical cells). To get an antiparallel director configuration, irradiation directions were antiparalel. The first type of cell was used to determine the direction of LC alignment whereas the second type was used to measure the pretilt angle on the plasma treated substrates. The cell gap was maintained with spacers of 6 μm and 20 μm in diameter. The cells have been filled with nematic LC K15 (5CB) by Merck.

The pretilt angle of LC alignment was measured in symmetrical cells using the crystal rotation technique. The azimuthal anchoring energy was determined from the experimentally measured twist angle in the combined cells.

3. Results and Discussion

3.1. Irradiation with Plasma Beam

3.1.1. Organic Substrates

The quality of LC alignment on the plasma treated substrates depends on the irradiation conditions. The in-plane alignment is poor for the angle of plasma incidence 0^0-15^0. The long time irradiation causes complete etching of the polymer coatings. On account of it, the irradiation time was short (τ_{exp}= 2.5 min) in the following studies. The variation of current density j= (0.5-40) μA/cm^2 and ion energy E= (200-1200) keV did not cause substantial change of the quality of LC alignment. Excluding conditions of poor alignment, the quality of LC alignment on the plasma treated substrates was high and comparable with the quality obtained with rubbing and photoalignment method. The easy axis

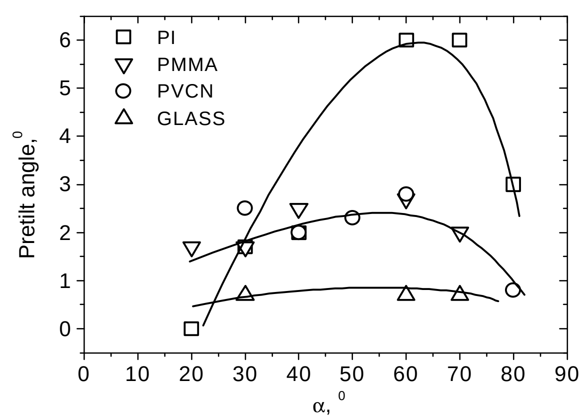

Figure 2. The LC pretilt angle vs plasma incidence angle curves for different substrates. The irradiation parameters for polymer and glass substrates are j=8μA/cm^2, E=600 eV, τ_{exp}=2.5 min and j= 0.5 μA/cm^2, E=400 eV, τ_{exp}=2.5 min respectively. The cells gap is 20 μm.

of LC alignment on all substrates coincides with projection of plasma beam on these substrates. The alignment is characterized by pronounced pretilt; the LC tilts towards the plasma beam. These properties are similar to those obtained in [4,5] for the ion beam irradiation. To test thermal stability of LC alignment on the plasma treated substrates, the cells were exposed to heat 90^0 over 30 h. The heating treatment did not cause any substantial change of alignment quality as well as a value of pretilt angle. The induced alignment is also photo-resistant; we did not observe any deterioration of LC alignment after irradiation of our cells with unpolirized UV light (15 mW/cm^2, 1 h).

The dependencies of pretilt angle θ versus incidence angles α for various polymer materials are shown in Fig.2. The θ vs α curves are non-monotonous. The maximal values of pretilt angle, θ_{max}, are observed at $\alpha=60^0$-70^0. The position of maximum of θ vs α curve slightly depends on material, j and E values. In contrast, θ_{max} substantially depends on these factors. The highest θ_{max} value is observed for PI substrates (about 6^0).

For PVCN and PMMA substrates $\theta_{max}=2.5^0$. The θ_{max} vs E and θ_{max} vs j curves for PI are presented in Fig. 3 and Fig. 4, respectively. Both of these dependencies go through maximum.

This behaviour can reflect a competition of surface alignment and randomisation processes initiated with plasma action. The latter process dominates at high energies, currents and exposure times, whereas the first one is essential at strongly optimised irradiation parameters. In our experiments, alignment with high LC pretilt is obtained at $\alpha=70^0$-80^0, j= 5-10 $\mu A/cm^2$ and E= 500-600 keV.

The azimuth anchoring energy W_a was estimated for all mentioned polymer coatings. The estimated value slightly dependant on aligning material is of the order of 10^{-3} erg/cm^2. So it has the same

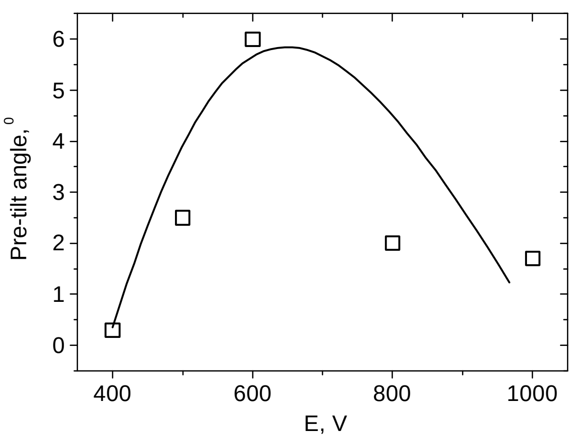

Figure 3. The pretilt angle of LC 5CB on polyimide substrates vs ion energy of Ar plasma beam. $j=8\mu A/cm^2$, $\tau_{exp}=2.5$ min, $\alpha=20^0$. Cell gap is 20 μm.

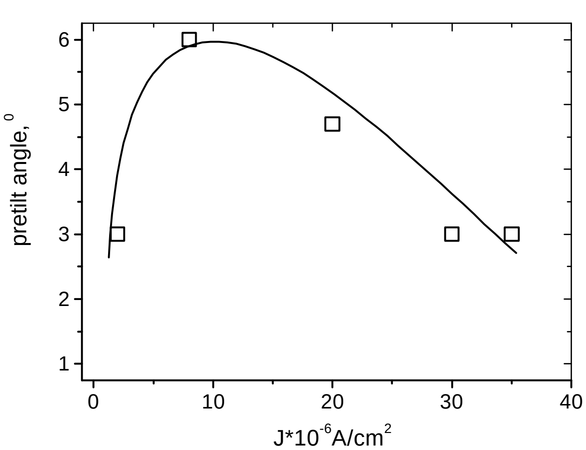

Figure 4. The pretilt angle of LC 5CB on polyimide substrates as a function of the current density of Ar plasma beam. E=600 eV, $\tau_{exp}=2.5$ min , $\alpha=20^0$. Cell gap is 20 μm.

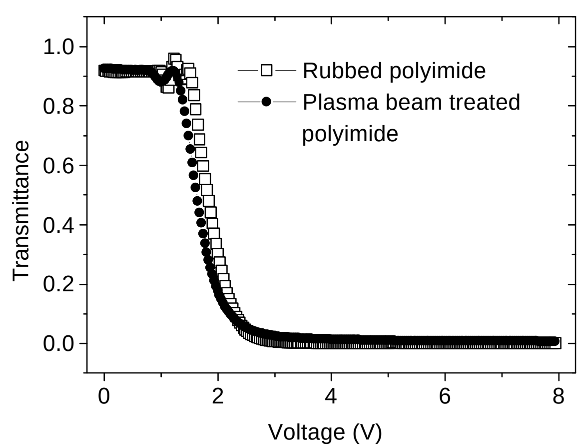

Figure 5. Light transmission vs applied voltage curves for TN cells made of rubbed polyimide (ð) and plasma beam treated polyimide (•) substrates. Plasma irradiation parameters: E=600V, j= 8 $\mu A/cm^2$, $\tau_{exp}=2.5$ min , $\alpha=20^0$). Thickness of both cells is 6 ± 0.2 μm.

order of magnitude as W_a obtained by photoalignment method [1]. The value of W_a was also estimated for various plasma incidence angles α. The W_a vs α dependence is non-monotonous. It reaches maximum at the values of α corresponding to maximum of θ vs α curve (Fig.2). This may imply that irradiation conditions corresponding to maximal anchoring also correspond to the maximal pretilt angle. Unfortunately, because of the big uncertainty of W_a measurements, the dependencies of W_a on current density j and ion energy E were not obtained. Using PVCN and PI, well-studied photoaligning materials, the efficiencies of photoalignment and plasma alignment methods were compared. As we admitted before, the value of anchoring energy in case of these methods is pretty much the same. At the same time, pretilt angle generated by plasma method is substantially higher then that for the phtoalignment (6^0 vs 0.5^0 for PI and 2.5^0 vs 0.3^0 for PVCN). In addition, photo- and thermally stability of the plasma induced alignment is substantially higher and it is more comparable with rubbed substrates. The one more important feature of the plasma method is possibility to overwrite alignment preliminarily induced.

It allows to reduce a number of masking steps in the process of cell patterning. Using single masking step several two-domain structures characterized by variation of easy axis and pretilt angle directions were developed. Electro-optic performance of the cells based on rubbing and plasma alignment method was compared. The light transmission T vs voltage V curves were measured for TN cells aligned by rubbing and plasma method. Fig. 5 shows that obtained T-V curves are very similar.

3.1.2. Non-Organic Substrates

As non-organic substrates we used bare glass and ITO covered glass slides. The quality of LC alignment on these substrates treated with plasma was comparable with that for the polymer substrates. However, the optimised irradiation conditions for the planar alignment differ from those for polymer coatings. Using irradiation parameters optimised for polymers, homeotropic alignment of LC 5CB was obtained. The planar alignment was reached at E=400 eV, j=0.5 $\mu A/cm^2$, and τ_{exp}=2.5 min. It is important to admit that ITO electrodes were not removed at these conditions. The maximal pretilt angle generated on both kinds of substrates was 0.5-0.7. It was only poorly dependant on the angle of irradiation (Fig.2).

3.2. Combination with Other Methods

As it was shown above, LC alignment in the cells based on plasma treated substrates is highly photo-stable. However, direct action of strong UV on the plasma treated substrates may modify its aligning properties. It concerns only photosensitive polymers. For instance, pretilt angle of 5B on plasma treated PVCN substrates was reduced from 2.5^0 to 1^0 by subsequent irradiation of the substrates with polarized UV light (10 mW/cm^2, 1 h). At the same time, azimuthal reorientation of the easy axis preliminarily induced by plasma was not realized by UV irradiation. Using plasma treatment, one can easily overwrite alignment written by UV irradiation or rubbing. Based on this, various patterning methods based on various types of LC alignment can be suggested. For instance, two-domain structures can be obtained by masking substrates, preliminarily aligned by UV or rubbed, and subsequent irradiation with plasma beam in a proper geometry. The cell having two-domain structure obtained by UV and plasma processing is presented in Fig.6. The directions of LC alignment in the domains are mutually perpendicular. The cells with the patterned pretilt angle were also produced.

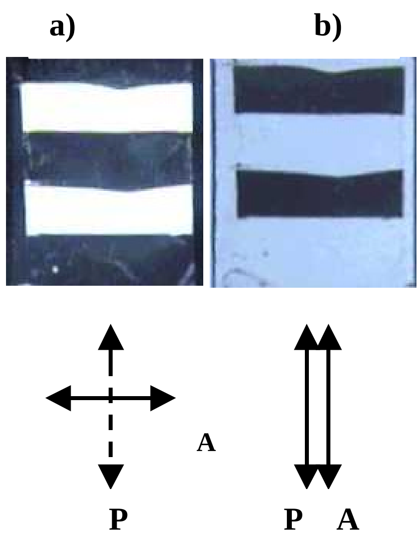

Figure 6. LC cell viewed between a pare of crossed (a) and parallel (b) polarizers. The cell is combined with rubbed PI substrate and PVCN substrate. The latter substrate is entirely irradiated with polarized UV light (I=6 mW/cm^2, τ_{exp} =15 min) and then with plasma beam (E=600V, j=10 $\mu A/cm^2$, τ_{exp} = 2.5 min, $\alpha=25^0$) through the mask. UV and plasma treatment generate mutually perpendicular directions of LC alignment.

4. Conclusions

Thus, oblique irradiation of the aligning substrates with a collimated beam of plasma is an effective method of LC planar alignment. It provides high quality LC alignment with a smooth control of pretilt angle and anchoring energy. The values of azimuth anchoring energy generated by plasma method are close to that obtained by photoalignment. On the other hand, the value of pretilt angle, photo and thermal stability of the alignment on plasma treated substrates are similar to those for rubbed substrates. The plasma method we considered is applicable to photosensitive and non-photosensitive, organic and non-organic surfaces. It can be used in combination with other methods of LC alignment, first of all for patterning of LC cells. This altogether shows the advance of this new non-contact method of LC alignment.

It is reasonably to compare plasma treatment procedure we considered with ion treatment method suggested by IBM group [4,5]. The characteristics of LC alignment obtained by these methods are quite similar. This may imply that ion component of plasma irradiation plays decisive role in the generation of surface anisotropy of the aligning substrates. On the other hand, some experimental facts confirm the action of other components on the aligning substrates. For instance, we detected considerable modification of the UV/Vis transmission spectrum of PVCN coatings. Most probably, this change is caused by UV irradiation of plasma penetrating in the bulk of film. One can expect that combination of various active components, which is realized in case of plasma treatment, may result in principally new aligning effects. In the present study we chose irradiation parameters similar to parameters used by IBM group. However, to our belief, the distinctive difference between ion and plasma treatment can be found by a wide-range variation of treatment parameters. These studies are in progress.

References

[1] M. O'Neill and S. M. Kelly, *J.Phys.D: Appl.Phys*., **33**, pp. 67-84 (2000).
[2] Y. Nano et al., *Proc.SID*, **31**, No4, 295 (1990).
[3] M. Hasegawa, *Jpn.J.Appl.Phys*., **39**, Part 1, No. 3A, 1272 (2000).
[4] P. Chaudhari, J. Lacey, S.A. Lien and J.Speidell, *Jpn.J.Appl.Phys*., **37**, Pt.2, N1-2, 55 (1998).
[5] P. Chaudhari, J. Lacey, J. Doyle, E. Galligan, S.A. Lien et.al. *Nature*, **411**, 56 (2001).
[6] J. Stoehr, M. Samant, J. Luening et al., *Science*, 392, 2299 (2001).
[7] Nakabayashi et al., US patent 5,710,608.
[8] M. Samant et al., US patent 6,313,896.
[9] N. Shahidsadeh et al. *Langmuir*, **14**, 6594 (1998).
[10] J. Fonseca, P. Charue, and Y. Galerne, *Mol.Cryst.Liq.Cryst*., **329**, 597 (1999).
[11] Y. Galerne, and P. Hubert, *Eur.Phys. B*, 8, 245 (1999).
[12] J. Dubois, M. Gazard, and A. Zann, *Appl.Phys.Lett*., **24**, 297 (1974).
[13] R. Watanabe, T. Nakano, T. satoh, H. Natoh, Y. Ohki., *JpnJ.Appl.Phys*., **26**, 337 (1987).
[14] O. Yaroshchuk, Yu. Zakrevsky, A. Dobrovolsky, S. Pavlov, *Proc. SPIE*, **4418**, 49 (2001).
[15] V. Zhurin, H. Kaufman, R. Robinson, *Plasma Sources Sci. Technol*., **8**, 1 (1999).