

## 20.4: Plasma Beam Etching Process for LC Alignment: Characteristics, Reliability and Topicality

**O. Yaroshchuk, R. Kravchuk, A. Dobrovolsky, I. Protsenko, A. Goncharov**

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

**C.D. Lee, P.C. Liu, C.Y. Lee,**

Industrial Technology Research Institute,

R436/B77, 195 Chung Hsing Rd., Sec.4, Chu Tung, Hsin Chu, Taiwan 310, R.O.C.

**O. D. Lavrentovich**

Liquid Crystal Institute and Chemical Physics Interdisciplinary Program, Kent State University, 44242 Kent, OH, U.S.A

**A. Muravski**

Institute of Applied Physics Problems, 220064 Minsk, Belarus

### Abstract

*We present brief overview of our new method of liquid crystal (LC) alignment based on the anisotropic etching of the alignment layers with a directed plasma flux. The method is realized by the use of anode layer source of "race track" geometry generating two "sheets" of accelerated plasma. These sheets are directed obliquely to the treated substrates. The static and dynamic irradiation regimes have been explored. This process provides liquid crystal alignment of planar, tilted and vertical types. The processing conditions and materials optimized for these types of LC alignment are discussed. A special attention is paid to the alignment stability and electro-optic performance. It is shown that the new method can be easily adapted for the alignment treatment of large area substrates used in the modern LCD manufacturing process.*

### 1. Introduction

The alignment of liquid crystals is one of the key issues of LCD technologies. The demands for the alignment toughen with the development of LCD. The requirements are to control both geometrical and energetical parameters of alignment, namely angular coordinates of easy axis and the anchoring energy, alignment uniformity and stability. The electrooptic performance sets additional requirements, such as strongly reduced residual DC (RDC) and acceptable voltage holding ratio (VHR), which partially relate to alignment process and alignment materials. In the modern LCD technologies, these requirements should be satisfied for Gen. 6 and Gen. 7 substrates with a size of 1500x1850 mm<sup>2</sup> and 1870x2200 mm<sup>2</sup>, respectively.

The traditional rubbing procedure that consists in unidirectional buffing of the alignment substrates is acceptable for substrates of moderate size, which do not require alignment patterning. However, the rubbing technique is hardly suitable for the substrates of last generations, first of all because of insufficient alignment uniformity. Besides, it is incapable of producing highly uniform alignment on the microscopic scale required for the projection type LCD. A new method of alignment is needed that would be capable to overcome the problems of rubbing. It should be easily scaled up and compatible with the patterning process. Also, it should considerably reduce the rejection rate.

Ion/plasma beam alignment processes are among the most promising candidates to replace the rubbing technique. In

spite of the long history of development in the field [1, 2], the interest to this technique sharply increased recently after the publications of IBM group [3,4]. The IBM approach implies substrate treatment with ions of low energy, which modifies the very top layer of the aligning film. At these conditions, destruction of the aligning films is minimized. In IBM experiments the flux of ions is created by an ion source of Kaufman type. This technique produces a high-quality alignment with controllable pretilt angle and strong anchoring achieved at different organic and inorganic alignment coatings.

We demonstrated recently [5,6] that similar high-quality alignment can be achieved by using a different type of the beam, namely, the beam of accelerated plasma generated by a special source, an anode layer thruster (ALT), known also as a source with a closed electron drift. The technique allows one to control the value and direction of the pretilt, thus yielding several new alignment modes [7,8].

In the present paper we characterize the alignment modes achieved with the ALT source, discuss the process and material issues, alignment stability and electro-optic performance. We also analyze potential of the new technique for the alignment treatment of large-area substrates. Finally we conclude that the technique might be very suitable for the modern LCD manufacturing process.

### 2. Alignment method

#### 2.1. Irradiation setup

The plasma processing for LC alignment has own history. It has been mainly experimented to control zenital anchoring energy and pretilt angle of LC [9-12]. In these experiments, the plasma lacked the needed directionality and thus the substrates needed to be rubbed before irradiation. Spokel and Gibson [13] reported planar/tilted LC alignment by processing alignment substrates with a *directed* plasma flux. In their experiments a modified RF plasma etcher was used, in which the reactive plasma was extracted and carried onto substrates by the gas stream. The energy of plasma ions was of the order of kT that is typical for "cold" plasma. In our approach, the plasma flux is extracted and accelerated *electrically*, which allows us to achieve ion energies of several hundreds eV, i.e., comparable to those in IBM experiments.

We used an anode layer thruster with a race track shape of discharge area. The basic scheme of this source is presented in Fig. 1. The source contains inner and outer cathodes and anode, which define the size and the shape of the discharge channel. The cathodes are grounded, while the anode is

under positive potential. At the outer cathode, the source contains permanent magnets. The magnetic circuit formed by steel body and cathodes is interrupted by the glow discharge gap. The particle flux is formed in the crossed

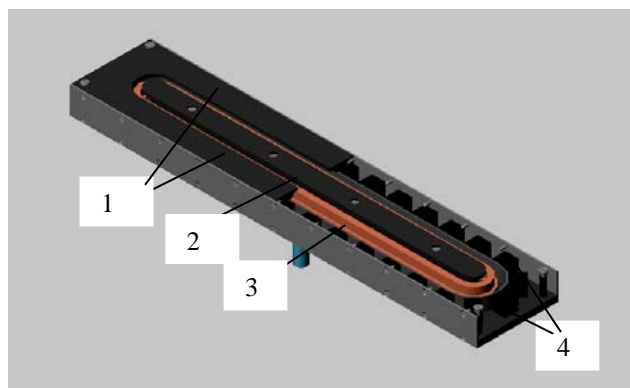


Fig. 1. ALT construction. 1 – outer cathodes; 2 – inner cathode; 3 – anode; 4 – permanent magnets.

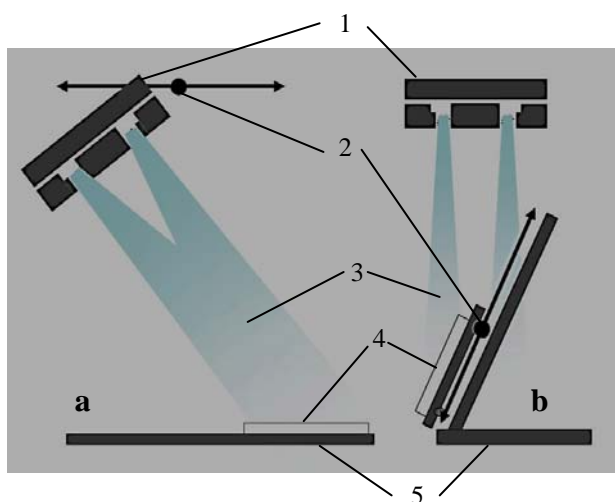


Fig. 2. The irradiation schemes. (a) source moving; (b) substrate's holder moving; 1 – ALT; 2 – moving direction; 3 – plasma “sheet”; 4 – substrate; 5 – substrate's holder.

electric and magnetic fields within the discharge channel.

In contrast to the Kaufman sources, ALT does not contain grids and hot elements (such as filaments and other secondary electron sources); the features thus simplify construction and substantially increase reliability. ALT can be optimized for the high efficiency of plasma extrusion that allows one to use it as thruster. This source was actually developed in the former Soviet Union as an engine for orbital correction of space satellites. It was also successfully adapted for the purposes of etching and sputtering deposition. The details of construction, characteristics and principles of operation of this device can be found elsewhere [14].

We used two ALT sources with different geometrical parameters. In the basic construction, the linear length of the “race track” was about 180 mm. In the scaled up ALT this length was 508 mm. The operation parameters of these two sources were rather similar. The gaseous feed was argon. It was let immediately in a vacuum chamber. The gas pressure  $p$  was  $(1-5) \cdot 10^{-4}$  Torr. The anode potential  $U$  was 300-3000 V. The ion current density  $j$  at the sample location

was  $0.5-20 \mu\text{A}/\text{cm}^2$ . The incident angle of plasma beam  $\phi$ , accounted from the surface normal, was  $70^\circ$ . The time of irradiation  $\tau_{\text{exp}}$  was varied from 0.5 to 20 min.

Both *static* and *dynamic irradiation regimes* were realized. In the static regime the source and the substrate are fixed, while in the dynamic mode either the substrate or the source moves, Fig.2. The speed of translation was 1-5 cm/s.

## 2.2. Alignment materials

We used a large number of organic and inorganic materials in plasma alignment tests. The organic materials were different kinds of polymers: polyimides (2555 from Dupont and SE150 from Nissan), PMMA, and others. For vertical alignment we used fluorinated polymers specially designed for this purpose. The polymers were dissolved in the appropriate solvents and then spin coated on either bare glass slides or the slides containing ITO electrodes. As inorganic materials we used bare glass, a-C:H and a-C:H:N coatings obtained by PECVD method, also  $\text{SiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$  and other coatings obtained by sputtering deposition. The modes of planar/tilted LC alignment realized by the plasma beam process are universal characteristics only weakly dependent on the material type. The opposite type

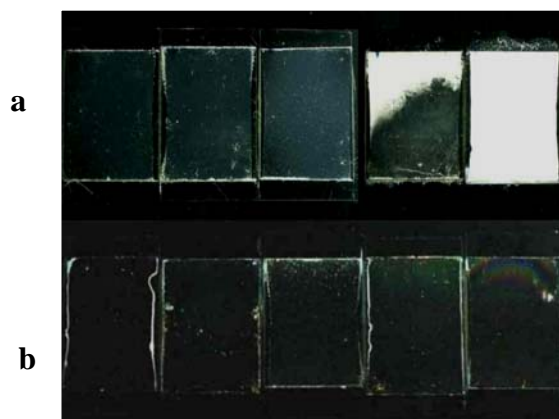


Fig. 3. The set of asymmetric cells viewed between two crossed polarizers. The tested PI substrates in the cells have been irradiated during 1, 2, 4, 6, 10 min (set (a)), and 1, 2, 10, 20, 40 min (set (b)), respectively. Irradiation conditions: cycling regime,  $\alpha=70^\circ$ ,  $j=8 \mu\text{A}/\text{cm}^2$ ,  $E=600 \text{ eV}$ . The cells are filled with LC 5CB ( $\Delta\epsilon>0$ ) (set (a)) and MJ961180 ( $\Delta\epsilon<0$ ) (set (b)).

of alignment, the vertical alignment (VA) mode, requires materials with enhanced hydrophobicity. The alignment stability is also sensitive to the material type. We discuss all these features in Section 2.4.

## 2.3. Alignment modes

A uniform alignment of the nematic liquid crystals in the cells with the plasma beam treated substrates is observed in a wide ranges of irradiation parameters:  $j=(0.5-30) \mu\text{A}/\text{cm}^2$ ,  $U=(200-2500) \text{ V}$ ,  $\tau_{\text{exp}}=0.1-30 \text{ min}$ . For liquid crystals with positive dielectric anisotropy ( $\Delta\epsilon>0$ ), used for TN and STN LCD, we have observed two modes of uniform LC alignment with different easy axis orientation. In the 1<sup>st</sup> mode, the easy axis is in the incident plane formed by the direction of beam and the normal to substrate. In the 2<sup>nd</sup> mode, the easy axis is perpendicular to the plane of incidence. These modes are observed in the static and both dynamic irradiation regimes described above. Figure 3 shows that the transition from the 1<sup>st</sup> mode to the 2<sup>nd</sup> mode occurs with the increase of irradiation time. A similar

transition is observed when one increases the current density of the Ar ions. In other words, the type of alignment is controlled by the irradiation dose.

Note that the 2<sup>nd</sup> alignment mode is apparently absent in the technique proposed by the IBM group [3, 4]. We also observed transient mode between the 1<sup>st</sup> and the 2<sup>nd</sup> alignment modes with the two-fold degenerated alignment. It was detected only in the static irradiation regime that provides continuous distribution of the exposure dose in the sample plane (because of Gaussian distribution of current density in the beam). It is worth mentioning that the sequence 1<sup>st</sup> mode – two-fold degenerated alignment – 2<sup>nd</sup> mode was earlier realized for the oblique deposition alignment [15]. This may be evidence of similar alignment mechanisms in case of these procedures.

Fig. 3 shows that at the processing parameters  $j = (3-30) \mu\text{A}/\text{cm}^2$ ,  $E = (400-1000) \text{ eV}$ , and  $\tau_{\text{exp}} = 1 - 20 \text{ min}$ , liquid crystals with  $\Delta\epsilon < 0$ , commonly used for VA, align only in the 1<sup>st</sup> mode. The pretilt angle is  $20^\circ < \theta < 45^\circ$ . However, at very low irradiation dose ( $j \leq 0.5 \mu\text{A}/\text{cm}^2$ ,  $E = (400-600) \text{ eV}$ , and  $\tau_{\text{exp}} \leq 1 \text{ min}$ ), on hydrophobic alignment layers, tilted vertical alignment can be realized [16].

## 2.4. Control of alignment parameters

The 2<sup>nd</sup> mode corresponds to planar alignment (pretilt angle is zero). In the 1<sup>st</sup> alignment mode, pretilt angle is nonzero in a general case. For LC with  $\Delta\epsilon > 0$ , it can be varied in the range of  $0^\circ-10^\circ$  with the exposure dose, incidence angle of plasma beam and ion energy [5,6]. The LC with  $\Delta\epsilon < 0$  shows alignment with  $20^\circ < \theta < 40^\circ$ . Both LC with  $\Delta\epsilon > 0$  and LC with  $\Delta\epsilon < 0$  may be aligned vertically (tilted VA) in case of hydrophobic surfaces providing homeotropic alignment before irradiation. The value of pretilt angle in case of VA can also be controlled with the parameters mentioned above [16].

The azimuthal anchoring energy  $W_a$ , in general case, is stronger in the 2<sup>nd</sup> mode. The order of magnitude of  $W_a$  is  $10^{-2}-10^{-1} \text{ erg}/\text{cm}^2$  (1<sup>st</sup> mode) and  $10^{-1}-10^0 \text{ erg}/\text{cm}^2$  in the 2<sup>nd</sup> mode. The anchoring transition from the 1<sup>st</sup> to the 2<sup>nd</sup> mode implies rotation of easy axis in  $90^\circ$ . This suggests original one-mask method of the alignment patterning [6].

## 2.5. Alignment stability

A serious problem of plasma beam alignment is the alignment aging. The alignment observed in the freshly prepared samples gradually degrades with a time of storage. The important reasons of this phenomenon are the following changes in the top layer of the aligning film: (1) appearance of low molecular weight (LMW) fraction of the alignment material and (2) generation of free radicals on the aligning substrates due to the bond scission with the plasma particles [17]. The LMW material may be partially dissolved in LC that results in the change of anchoring conditions. In turn, free radicals may react with LC on the LC-substrate interface also changing boundary conditions. As we ascertained, the aging processes can be effectively suppressed by the material selection and processing optimization.

Figure 4 and Figure 5 show aging curves of pretilt angle  $\theta$ , and twist angle  $\phi$  in the antiparallel and  $90^\circ$  TN cell, respectively. The results are presented for PI and a-C:H films equally treated. On the PI aligning films,  $\theta$  shows full decay within several months of storage. In parallel,  $\phi$ , as a measure of azimuthal anchoring strength, gradually decreases. In contrast, on a-C:H substrates,  $\theta$  and  $\phi$  are rather stable. This difference may be caused by the substantial difference in the concentration of chemical bonds; the bonds concentration is substantially higher in

case of strongly crosslinked a-C:H film as compared with the films of linear polymers: the high density of bonds in a-C:H films hampers formation of LMW fraction.

To reduce aging, authors of [17] suggested passivation of the aligning films. In their procedure, after anisotropic etching with Ar ion beam, the substrate is exposed to the molecular hydrogen obtained by the dissociation of  $\text{H}_2$  molecules. The dissociation was thermally stimulated by the

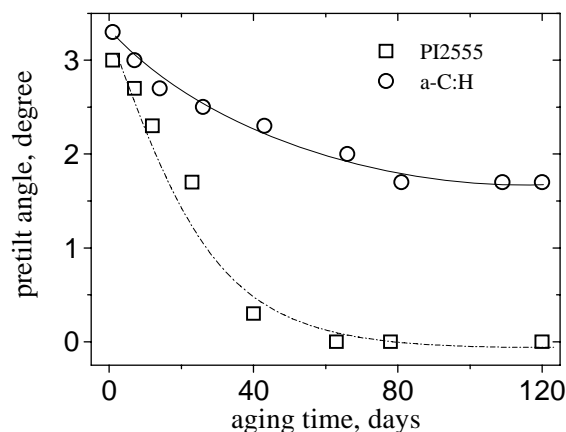


Fig. 4. The pretilt angle vs. cell aging time for the 5CB antiparallel cells with PI2555 and a-C:H alignment substrates equally processed by plasma beam. Room conditions.

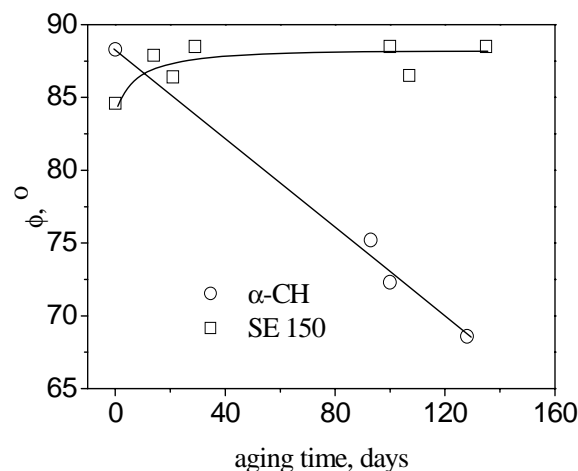


Fig. 5. The twist angle vs. aging time curves for the  $90^\circ$  TN cell filled with ZLI2293. The alignment coatings are a-C:H and PI SE150 equally processed by plasma beam. Room conditions.

red-hot wolfram filament placed in the vicinity of the treated substrate. The chemically active atoms of hydrogen react with the free radicals from the alignment film causing its neutralization. In our procedure, the alignment and passivation treatments can be combined, if the  $\text{Ar}/\text{H}_2$  mixture is used as a gaseous feed. By this way we obtained substantially stabilised LC alignment. This means that plasma flux contains sufficient amount of atomic hydrogen to realize passivation. It is noteworthy that atomic hydrogen is directed at the substrate that should increase efficiency of passivation.

In spite of sufficient progress, more studies are needed to completely overcome the problem of the alignment aging.

### 3. Electrooptic performance

The transmittance vs. voltage (T-V) curves were measured for the low-pretit TN cells and VA TN cells. There is no noticeable difference between T-V curves of these cells and the cells based on the standard procedures (rubbing and  $S_iO_2$  oblique deposition, in case of low tilt TN cell and VA TN cell, respectively). Thus T-V characteristic are insensitive to the alignment method.

Table 1.

	PI rubbing	PI Ar plasma	PI Ar/H <sub>2</sub> plasma
VHR, %	96.4	96.2	96.6
RDC, V	0.096	0.102	0.090

The VHR and RDC data are presented in Table 1. One can conclude that VHR/RDC parameters of LC cells based on PI layers subjected to rubbing and plasma beam alignment are rather similar. One can also see that addition of H<sub>2</sub> to the Ar feed may considerably reduce RDC used as a measure of image sticking. Thus, substitution of rubbing by plasma beam alignment process does not worsen electro-optic performance of LC cells. Moreover, it gives the way to improve some parameters, such as VHR/RDC.

### 4. Extension to the large area substrates

In these studies, we used ALT with extended linear part (the width of plasma 'sheet' was about 508 mm). The low power operation regime in the alignment processing eliminated the need in cooling lines. It lightened the source and allowed us to avoid the use of hoses supplying cooling liquid, thus increasing reliability.

The width of plasma "sheet" limits the width of the treated substrates. To study treatment uniformity on these substrates, we used mosaic principle: the large substrates were substituted with the substrates of smaller size (20x30 mm<sup>2</sup>) placed in different parts of 450x450 mm<sup>2</sup> holder plate. The substrates were irradiated in the dynamic regime (the moving velocity about 2 cm/s). For the irradiation times longer than the time of one translation cycle, the in-plane alignment directions for different substrates were pretty much the same; the variation of easy axis is within 1° and it even decreases with the number of translation cycles. To check the out-of-plane uniformity, we compared the values of LC pretilt angle on the 20x30 cm<sup>2</sup> substrates. The variation in pretilt angle for the substrates from different places of holder was within 20 %, in both low tilt alignment (1<sup>st</sup> mode) and high tilt alignment (VA) mode. The two methods of translation (source translation and substrate translation, Sec.2.1) result in very similar alignment, including excellent alignment uniformity. At the same time, in the industrial units, we prefer to translate source and keep the substrate fixed to reduce damage risk of the large area glass substrates.

### 5. Conclusions

In summary, the anisotropic plasma beam etching procedure, at optimized conditions, yields highly uniform and stable LC alignment with controllable easy axis and anchoring strength. The method can be effectively used to realize low tilt alignment for TN and IPS modes, and high tilt alignment for VA LCD mode. The electro-optic parameters of LC cells based on the plasma beam alignment procedure are rather similar to those of the cells treated by

rubbing. The plasma beam alignment method is kindred to the method of ion beam alignment. The alignment mechanisms in case of these processes seem to be the same. At the same time, plasma beam alignment realized on the base of anode layer thruster allows one easily to extend the alignment treatment to large area substrates, including substrates of the last generation. Also, it allows to simplify other processes, e.g., alignment layer passivation.

Since the ALT sources can also operate in the sputtering mode, one can combine film deposition and alignment etching processes in the same industrial unit. Moreover, the described plasma processes are compatible with the vacuum processes used for the deposition of driving circuits. This suggests a "dry" process for the manufacturing of LCD substrates. Based on these results, one can also predict vacuum line of LCD production with reduced demands to room conditions and minimized human interference in the technological process. The features outlined above allow us to conclude that plasma/ion beam processing may successfully replace traditional rubbing procedure in the next generations of LCD.

### 6. Acknowledgement

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