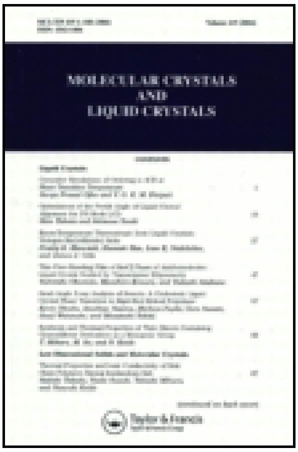

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Plasma Beam Alignment of Liquid Crystals on the Bare Glass: Modification of Surface Chemical Composition

R. Kravchuk [a], K. Artyushkova [b] & O. Yaroshchuk [a]

[a] Institute of Physics, NASU, Kyiv, Ukraine

[b] Department of Chemical and Nuclear Engineering, University of New Mexico, Farris Engineering Center, Albuquerque, NM, USA

Version of record first published: 16 Jun 2011

To cite this article: R. Kravchuk, K. Artyushkova & O. Yaroshchuk (2011): Plasma Beam Alignment of Liquid Crystals on the Bare Glass: Modification of Surface Chemical Composition, Molecular Crystals and Liquid Crystals, 546:1, 79/[1549]-86/[1556]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.571923

Mol. Cryst. Liq. Cryst., Vol. 546: pp. 79/[1549]–86/[1556], 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.571923

Taylor & Francis
Taylor & Francis Group

Plasma Beam Alignment of Liquid Crystals on the Bare Glass: Modification of Surface Chemical Composition

R. KRAVCHUK,[1] K. ARTYUSHKOVA,[2] AND
O. YAROSHCHUK[1]

[1]Institute of Physics, NASU, Kyiv, Ukraine
[2]Department of Chemical and Nuclear Engineering, University of New Mexico, Farris Engineering Center, Albuquerque, NM, USA

X-ray Photoelectron Spectroscopy was applied to study the chemical composition of the modified glass surfaces by the flux of accelerated Ar or Ar/H_2 plasma in order to clarify mechanisms of liquid crystal (LC) alignment on these surfaces. It was established that the surface of prinstine glass exposed to air contains carbonaceous contamination layer consisting of about 50% of aliphatic/aromatic carbon and about 50% of C–O moieties of various types. Plasma processing results in partial ablation of this layer and modification of its chemical composition. This suggests that LCs are actually being aligned by the plasma modified carbonaceous layer rather than by a pure glass.

Keywords Alignment; carbonaceous layers; liquid crystal; plasma treatment; XPS

1. Introduction

Liquid crystal (LC) alignment is among the major problems of modern liquid crystal devices. To date, the traditional rubbing technique is unable to satisfy increasing demands for the LC alignment. This situation stimulates development of alternative alignment methods. Recent years were marked by the great interest to so called ion/plasma beam alignment, which has shown high efficiency for LCs [1–8] and reactive mesogens [9]. The essence of the method is that surfaces treated by ion or plasma beams from oblique angle develop an ability to align LCs. In contrast to traditional rubbing technique, this method provides excellent microscopic alignment homogeneity, easy way for the alignment pattering, and applicability for curved surfaces. Furthermore, the unique feature of this technique is that presence of alignment layer is optional; *i.e.*, LC can be aligned directly on bare substrates, *e.g.*, glass, silicon, plastic, *etc.* [7–9].

Address correspondence to O. Yaroshchuk, Institute of Physics, NASU, prospekt Nauki 46, 03028 Kyiv, Ukraine. Tel.: 380 44 5252424; Fax: 380 44 5251589; E-mail: olegyar@yahoo.com

As it is known, LC alignment on surfaces is caused by anisotropy of these surfaces. In case of ion or plasma beam alignment this anisotropy arises due to the fact that irradiation beam is coming from the angle to the surface. According to the literature, particles bombarding the surface affect this surface in two ways. The study of the treated surfaces by the near edge absorption fine structures (NEXAFS) method and X-ray photoelectron spectroscopy (XPS) revealed angularly selective depletion of the surface molecular bonds [10–12]. Aromatic rings are the most vulnerable fragments on such surfaces, that is, the best target for the accelerated particles. The rings whose plane is oriented perpendicular to the flow of particles are subjected to the most sever destruction. In turn, the rings and linear fragments oriented towards the particle beam are subjected to the least destruction and determine direction of LC alignment.

Moreoever, studies using AFM revealed the anisotropy of the topography of the treated surfaces [7,13]. It was noticed that LC always aligns in the most smooth direction that corresponds to a general empiric rule formulated in Kumar's works [14,15] substantiated by a free energy minimization principle [16].

The above results mainly relate to the films of organic materials and diamond like carbon. However, besides these materials, after particle beam processing clear alignment effect demonstrate classical inorganic materials, such as SiO_2, ZnO, Ta_2O_5, Fe_2O_5 and the like. These materials in their pure form do not contain complex fragments, which can be considered as in above to be the main targets for the damage/removal by accelerated particles. This suggests that the mechanism of induced anisotropy on the surface of such materials has some specificity. Seo *et al.* [17] suggested that aligning effect in case of inorganic oxides is caused by the angularly selective breaking of El-O bonds (El = Si, Zn, Ta, Fe, Al, etc.).

In the present paper we consider specificity of aligning mechanisms on the glass surface. We have detected carbonaceous layer on the glass surface and discovered its important role in LC alignment. The change of chemical composition of this layer under plasma processing is also investigated.

2. Experimental

As glass samples, we used microscope slides from Fisher Scientific stored in atmosphere. The samples were washed in distilled water with detergent and then thoroughly rinsed with a high-purity isopropyl alcohol and distilled water in ultrasonic bath. After drying in desiccator at 120°C over 2 hours, the samples were treated in vacuum by the flux of plasma generated by anode layer source. The working gas was argon or the mixture of argon with hydrogen (2:1). The working pressure was $4–5 \cdot 10^{-4}$ torr and the anode potential was 900 V. This corresponded to the current density in the plasma beam of about $6\,\mu A/cm^2$. The plasma beam was set at the angle 70° to the normal of substrate. The exposure time was 4 min. During irradiation, the glass slides were moved under the plasma beam in back-forward direction with a speed ~ 2 cm/min. This scanning regime ensured multiple exposures of the sample under the plasma beam and thus homogeneity of surface treatment.

X-ray photoelectron spectroscopic analyses of the glass samples was done using Kratos Analytical AXIS Ultra Spectrometer with an Al K-α X-ray source operating at 300 W. The base pressure was $2 \cdot 10^{-10}$ torr and the operating pressure was $2 \cdot 10^{-9}$ torr. Charge neutralization was used for all samples to prevent charge accumulation. Three areas per sample were analyzed. The low resolution (survey) and high

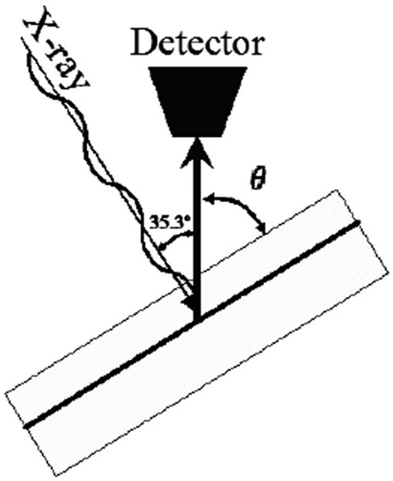

Figure 1. The layout of XPS experiment.

resolution spectra were acquired at pass energies of 80 and 20 eV and step size of 1 and 0.1 eV, respectively. In the acquisition of high energy resolution spectra take-off angles θ of 90°, 60° and 20° were utilized (see Fig. 1). They correspond to ~10, ~8, ~3 nm of the sampling depth. Data analysis and quantification were performed using CasaXPS software. A linear background subtraction was used for quantification. All the spectra were charge-referenced to aliphatic carbon at 285.0 eV. A 70% Gaussian/30% Lorentzian line shape was utilized in the curve-fit. Curve-fitting was carried out using individual peaks of constrained width and shape.

3. Results and Discussion

Table 1 presents elemental composition of the top surface layer of glass before and after plasma beam irradiation for three different sampling depths. Elements were quantified as percentages of the total atomic concentration of all elements present in the analyzed surface layer.[1] The following features can be seen.

(1) All glass samples, including untreated one, have surface elemental composition substantially different from the theoretical one. The presence of large amounts of carbon is especially evident, and this concentration increases at shallower depths. This means that the carbonaceous layer is located in the uppermost part of the glass slides. According to [18,19], this contamination layer is formed due to adsorption of carbon from atmosphere. Its concentration on the surface of the glass is a function of the air exposure time and reaches 50% for long exposures [19]. The carbon contamination starts immediately after entering the glasses into the air and the rate of this process is much higher in the first minutes of the exposure as compared to that afterwards. One can assume that glass cleaning procedure (use of detergents, organic solvents, *etc.*) may also contribute to formation of this layer.

(2) The concentration of surface carbon considerably reduces after the plasma exposure. This means that the uppermost part of the carbonaceous layer is removed

---

[1] The elements presented in glass in small quantity (B, Ca, etc.) were below detection limit.

Table 1. Elemental content of the surface layer of glass before and after plasma beam exposure. The data are presented for three different testing depths

	d = 10 nm				d = 8 nm				d = 3 nm			
Element sample	C, %	Na, %	O, %	Si, %	C, %	Na, %	O, %	Si, %	C, %	Na, %	O, %	Si, %
Untreated glass	33.6	4.2	45.5	16.7	34.6	4.2	44.8	16.4	44.4	4.1	38.3	13.2
Ar plasma treated glass	23.7	6.5	52.9	16.9	26.5	5.1	51.8	16.5	42.7	4.1	40.7	12.4
Ar/H_2 plasma treated glass	22.0	6.3	54.5	17.2	24.2	5.3	53.4	17.1	37.1	4.6	43.8	14.5

due to plasma etching. A slight increase in oxygen concentration can be caused by oxidation of reactive species that appears during plasma treatment as a result of the exposure of the treated samples to the atmosphere.

More information about the transformation of the surface layer was derived from high resolution spectra. To elucidate the chemical state of carbon atoms in this layer, C 1 s spectra were carefully analyzed. The C 1 s curve fitted spectra for unexposed glass and the glass processed by Ar plasma are presented in Figure 2. One can see that the spectra are fitted well with 7 symmetrical peaks. The binding energies of these peaks are characterized in Table 2. There is evident that contamination on pristine glass consists of about 50% of aliphatic/aromatic carbon and about 50% of C–O moieties of various types (C–OH, C–OC, C–O–C=O, *etc.*). The plasma treatment, irrespective of feed gas, causes significant conversion of aromatic carbons into C–O species and carbide/graphite forms. Interestingly, the aliphatic carbon remains practically intact. This result suggests that, due to the presence of contamination layer, the main mechanism of induced anisotropy on the glass surface may be the same as that on surfaces of organic materials. As pointed above, it consists in selective destruction of organic bonds, first of all aromatic rings.

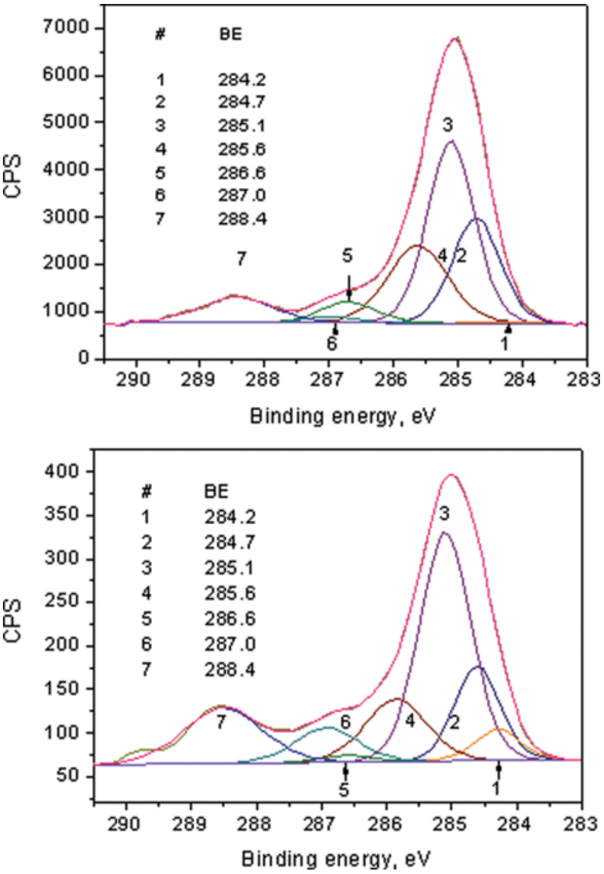

Figure 2. High resolution C 1 s spectra of (a) unexposed glass and (b) Ar plasma treated glass. Each spectrum is curve fitted using 7 peaks listed in Table 2.

Table 2. Carbon species presented in the surface layer of glass and their percentage before and after plasma beam exposure

	Peak position, eV						
Specification sample	Carbide/graphitic 284.2	Aromatic 284.7	Aliphatic 285.1	C^*-CO 285.6	$C-O-C$ 286.6	$C-OH$, $C^*-O-C=O$ 287.0	$C-O-C^*=O$ 288.4
Pristine glass	1.1	24.5	39.2	19.3	6.3	1.2	8.4
Glass treated with Ar plasma	4.6	15.6	42.4	12.3	3.6	5.9	15.6
Glass treated with Ar/H_2 plasma	3.1	14.0	37.5	17.8	6.9	5.7	15.1

[a] The asterisk designates the atom for which the binding energy is estimated.

Anisotropy of the in-plane distribution of such fragments can be detected by measuring the high resolution spectra at different rotation angles of the sample relative to its axis. At this stage, we did not study it, as it requires very time-consuming experimental procedure [12]. However, surface anisotropy of the treated glasses was earlier clearly detected in AFM tests [6]. It was found that the glass surface treated under conditions as in the present study shows clear topological anisotropy with the smoothest relief in the direction parallel to the projection of plasma beam on the surface. In accordance with Kumar's empiric rule [14,15], LC chose this direction for alignment.

The obtained results also lead to the conclusion that LC is aligned on the carbonaceous contamination layer rather than on glass. In a sense of LC alignment, this layer is similar to the a-C:H coatings and even the films of polymeric hydrocarbons, since the contamination layer is largely composed of organic components. This intermediate layer seems to be responsible for planar LC alignment realized on the glass processed by plasma beam.

4. Conclusions

We have discovered an important role of the carbonaceous contamination layer, formed on the glass surface upon the exposure of air, in alignment of LCs. The plasma processing of glass modifies this layer and induces in it anisotropy. This modified layer is an actual alignment layer for LCs. It is known that carbonaceous contamination forms on the surfaces of various materials exposed to air. On this basis one can assume that this layer plays an important role in LC alignment on various inorganic surfaces that is discovered mechanism is quite general.

Acknowledgment

Part of these studies was conducted under the project 10/07-H (NASU, Ukraine).

References

[1] Chaudhari, P., Lacey, J., Lien, S. A., & Speidell, J. (1998). *Jpn. J. Appl. Phys.*, *37*(1), L55.

[2] Chaudhari, P., *et al.* (2001). *Nature*, *411*, 56.

[3] Hwang, J. Y., Jo, Y. M., Seo, D. S., Rho, S. J., Lee, D. K., & Baik, H. K. (2002). *Jpn. J. Appl. Phys.*, *41*, L654.

[4] Gwag, J. S., Park, K. H., Kang, D. J., Jhun, C. G., Kim, H., Cho, S. J., Yoon, T. H., & Kim, J. C. (2003). *Jpn. J. Appl. Phys.*, *42*, L468–471.

[5] Fulghum, E., Su, L. L., Artyushkova, K. J., West, L., & Reznikov, Y. (2004). *Mol. Cryst. Liquid Cryst.*, *412*, 1971.

[6] Yaroshchuk, O., Zakrevskyy, Y., Dobrovolskyy, A., & Pavlov, S. (2001). *Proc. SPIE*, *4418*, 49.

[7] Yaroshchuk, O., Kravchuk, R., Dobrovolskyy, A., Qiu, L., & Lavrentovich, O. D. (2004). *Liq. Cryst.*, *31*(6), 859.

[8] Yaroshchuk, O., Kravchuk, R., Dobrovolskyy, A., Liu, P. C., & Lee, C. D. (2005). *SID, J.*, *13/4*, 289.

[9] Yaroshchuk, O., Parri, O., Kravchuk, R., Satayesh, S., & Reijme, M. (2008). *SID, J.*, *16*(9), 905.

[10] Stoehr, J., Samant, M. G., Luening, J., Callegari, A. C., Chaudhari, P., Doyle, J. P., Lacey, J. A., Lien, S. A., Purushothaman, S., & Speidell, J. L. (2001). *Science*, *292*, 2299.

[11] Kim, J. B., Kim, K. C., Ahn, H. J., Hwang, B. H., Hyun, D. C., & Baik, H. K. (2007). *Appl. Phys. Letters*, *90*, 043515.

[12] Pylypenko, S., Artyushkova, K., & Fulghum, J. E. (2010). *Applied Surface Science*, *256*, 3204.

[13] Lin, S. S., & Lee, Y. D. (2006). *Jpn. J. Appl. Phys.*, *45*, L708.

[14] Cull, B., Shi, Y., Kumar, S., & Schadt, M. (1996). *Phys. Rev. E*, *53*, 3777.

[15] Kumar, S., Kim, J. H., & Shi, Y. (2005). *Phys. Rev. Lett.*, *94*, 077803.

[16] Berreman, D. (1972). *Phys. Rev. Lett.*, *28*(26), 1683.

[17] Oh, B. Y., Lee, D. K., Kim, Y. H., & Seo, D. S. (2009). *J. Appl. Phys.*, *105*, 054506.

[18] So, L., Ng, N., Bilek, M., Pigram, P. J., & Brack, N. (2006). *Surf. Interface Anal.*, *38*, 648.

[19] Jang, H. K., Whangbo, S. W., Choi, Y. K., Jeong, K., Whang, C. N., Wang, C. H., Choi, D. J., & Lee, S. (2001). *J. Non-Crystalline Solids*, *296*, 182.