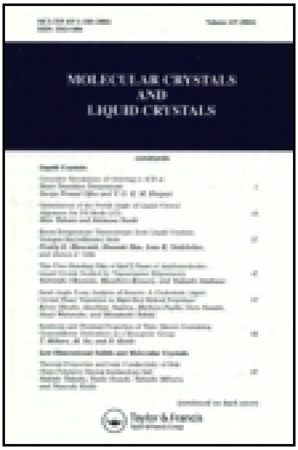

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Aging of Liquid Crystal Alignment on Plasma Beam Treated Substrates: Choice of Alignment Materials and Liquid Crystals

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We studied temporal degradation (aging) of liquid crystal (LC) alignment on plasma beam processed substrates using LC pretilt angle as a measure of this process. It was shown that aging may manifest itself either in pretilt angle decay or pretilt angle growth depending on LC and alignment material. The alteration of electro-optic curves due to alignment aging was revealed. The weakest aging effect was observed for inorganic alignment layers obtained by PECVD method. An important reason of aging is chain scission and generation of low molecular weight reactive species disturbing surface anisotropy of atomic bonds and anisotropy of surface topology.

Keywords: alignment aging; ion beam alignment; liquid crystal alignment; PCVD; sputtering

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1. INTRODUCTION

The anisotropic etching of the liquid crystal (LC) alignment substrates by an obliquely incident ion/plasma beam is among the most effective and practical processes for low-pretilt LC alignment [1–5]. The high alignment uniformity on both the microscopic and macroscopic scales, the wide variation range of pretilt angle and anchoring energy, simple pattering procedure and the possibility of aligning LC on practically any material are indisputable advantages of this alignment method. However, its practical utilization is hindered by several intrinsic problems with the most serious one known as alignment aging. This consists in a gradual weakening of anchoring strength and change of pretilt angle over the time of sample storage [6–9]. Often these changes are invisible to the eye, but can be easily detected by the methods of pretilt angle and anchoring energy measurements. In some cases, however, anchoring strength degrades strongly so that it is clearly evident in degradation of LC alignment.

The nature of the alignment degradation is not yet completely clear. One of the most probable reasons, discussed in Ref. [6], is reactivity of the treated surface. According to this concept, the accelerated ions bombarding alignment substrates cause bond scission and formation of free radicals on the surface. Further, these radicals react with a LC in the boundary layers of the LC cell, changing boundary conditions and so bulk LC alignment maintained by the substrates. To diminish surface reactivity, the authors of [6] proposed an additional process – passivation of ion beam treated substrates by atomic hydrogen. The reactively active atomic hydrogen neutralizes free radicals, forming covalent bonds with them. This passivation principle is very similar to that which is used in stabilization of solar batteries [10].

As we further considered, alignment aging can be radically weakened by a proper choice of alignment materials [7–9]. It was shown that coatings prepared by plasma deposition demonstrate much more stable alignment than coatings on a base of synthetic polymers. In the present paper we confirm this rule considering a bigger choice of materials and methods of their deposition. Besides, efficiency of aging for different kinds of LC was also studied. It is shown that aging depends strongly on LC content and proves itself differently for different LC. The possible aging mechanisms are discussed.

2. EXPERIMENTAL

2.1. Alignment Materials

As alignment materials we used several types of materials.

(1) Polyimide (PI) 2555 commercially available from Dupont. The PI films were spincoated on glass/ITO slides and subsequently backed at 220°C over 2 h. The substrates were manually rubbed by a velvet cloth.

(2) SiO_x coatings obtained by PECVD and sputtering deposition methods. The PECVD layers were obtained in a glow discharge of SiH_4 and O_2 gases by using r.f. reactor KAI1 from Balzers. The sputtering deposition was carried out by the anode layer ion source of sputtering type designed by Izovac. In this experiment the vitreous silica target was bombarded by an Ar beam. The extracted atoms of target were directed to the substrate at normal incidence. The details of this process can be found in our previous papers [11–12].

(3) a-C:H coatings produced by PECVD and sputtering deposition methods. For the PECVD we used home made parallel plate reactor with r.f. capacitively coupled glow discharge [13]. The sputtering deposition was carried out by sputtering device used for deposition of SiO_x films. The target was a graphite and the gas feed was a mixture of Ar and CH_4 (2:1) [12].

2.2. Alignment Process

The alignment treatment of the substrates was ion milling. It was performed by the beam of ions or, more precisely, accelerated plasma, from the anode layer source with a race track shape of discharge area. This process was thoroughly optimized in the previous work [7–9, 11–13]. The processing gas was argon. The substrates were placed obliquely with respect to an ion "sheet" on the moving platform as is depicted in Figure 1. The incidence angle of the ion flux, accounted from the substrate's normal, was 70°. The anode potential determining maximal energy of ions was 600 V, the current density in the sample position was 5–7 $\mu A/cm^2$. The substrates were processed over 5 min in the cycling translation regime. The velocity of translation was 4 mm/s. These treatment conditions provided excellent alignment of all LC mixtures on all alignment layers listed below.

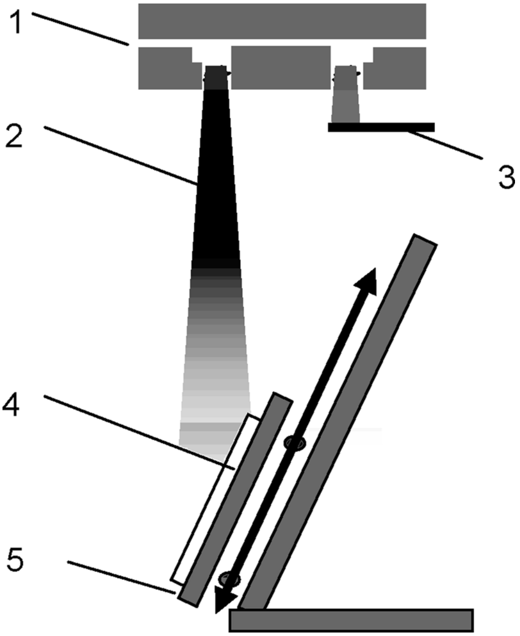

FIGURE 1 The scheme of irradiation setup: 1 – source; 2 – plasma "sheet"; 3 – shutter; 4 – substrate; 5 – substrate's holder.

2.3. Cells and Alignment Evaluation Techniques

For the pretilt angle measurement we used standard antiparallel sandwich cells with a cell gap of 20 μm containing alignment layers of the same sort. The cells were filled with nematic mixtures ZLI2293, E7, E63 and TL205 obtained from Merck and thoroughly glued with epoxy adhesive to prevent contact of LC with atmosphere. As a measure of alignment degradation we used pretilt angle, which is the most sensitive to this process. The pretilt angle was measured by common crystal rotation procedure. The glued cells were stored at ambient conditions over a long time (longer than one year). The pretilt angle in these cells was monitored.

In parallel, we produced 90° TN cells on the base of the same alignment substrates. The thickness of TN cells was about 6 μm. These cells were used to observe changes in electro-optic performance corresponding to alignment aging. The transmittance-voltage curves of the cells placed between a pair of crossed polarizers were measured using the home made computerized system described in [14].

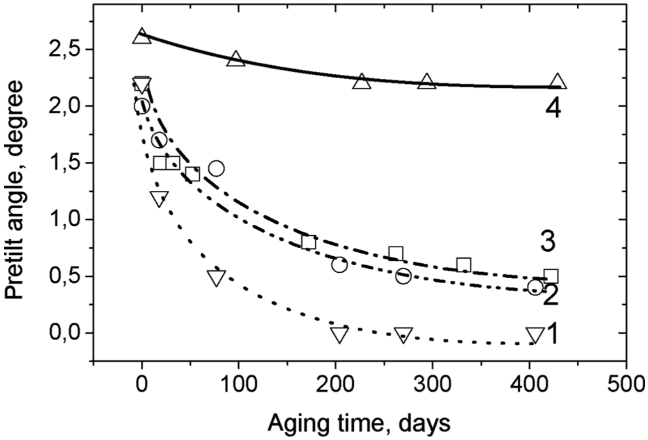

FIGURE 2 Pretilt angle vs. aging time curves for the antiparallel LC cells filled with ZLI 2293. The cells comprise different alignment layers: plasma beam processed layers of PI 2555, a-C:H and SiO_x (curves (1), (2), and (3), respectively) and rubbed PI 2555 layers (curve (4)). The a-C:H and SiO_x coatings are obtained by PECVD.

3. RESULTS

3.1. Pretilt Angle Decay

First we consider results for nematic mixture ZLI2293 routinely used in our previous alignment tests. Figure 2 shows pretilt angle aging curves for this LC aligned with different substrates. One can observe cardinal difference in aging curves for rubbed and plasma beam processed polyimide substrates. While the pretilt angle is rather stable on the rubbed PI, it gradually decreases to zero on the plasma treated PI. The pretilt angle decay process is considerably decelerated on a-C:H and SiO_x alignment layers obtained by PECVD method.

Comparing a-C:H and SiO_x alignment layers produced by plasma deposition and sputtering deposition one can conclude that PECVD method provides coatings considerably more resistant to ageing than the sputtered ones. For SiO_x films this is readily apparent from Figure 3. It is evident that the pretilt angle on sputtered SiO_x alignment layers approaches zero considerably faster than on the SiO_x layers obtained by PCVD method. The same tendency was detected for a-C:H coatings.

Figure 4 demonstrates pretilt angle aging on plasma beam processed polyimide substrates measured for two other liquid crystals. Surprisingly, in contrast to LC ZLI2293, pretilt angle of LC E63 grows. The pretilt angle of LC TL205 behaves in a similar manner. This

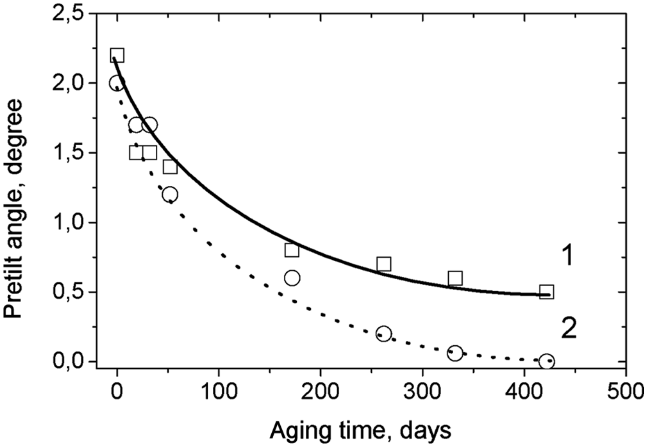

FIGURE 3 Pretilt angle vs. aging time curves for the antiparallel LC cells filled with ZLI 2293. The alignment layers in case (1) and (2) are SiO_x coatings obtained by PECVD and sputtering deposition, respectively.

unusual behavior was observed only for PI substrates, while for a-C:H and SiO_x substrates the aging curves were similar to those obtained for LC ZLI2293. The pretilt angle of LC E7 shows just insufficient decay for the monitoring period of 200 days.

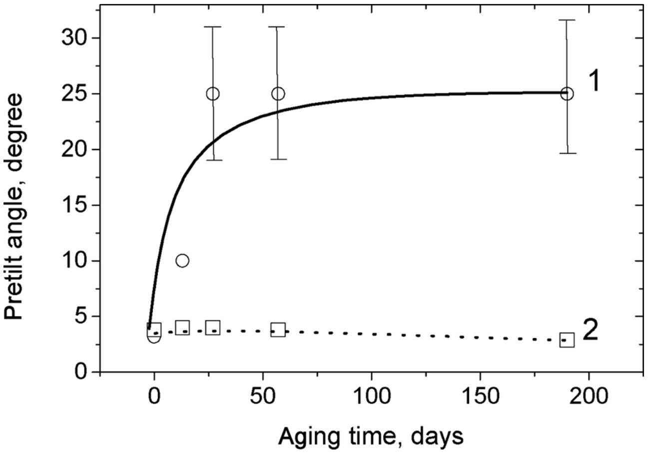

FIGURE 4 Pretilt angle vs. aging time curves for the antiparallel LC cells based on plasma beam treated PI 2555 substrates. The cell is filled with LC E63 (1) and E7 (2).

From the results above the following conclusions can be drawn.

1. Manifestations of aging are much diverse than we conceived before. The aging may reveal itself in pretilt angle decay (ZLI2293 on PI2555, a-C:H and SiO_x) and in the pretilt angle growth as well (E63 and TL205 on PI2555). The aging tendency depends on both LC and alignment layer.
2. The plasma coatings provide much better alignment stability than the conventional alignment films of synthetic polymers.
3. The plasma coatings are considerably more resistant to aging than the sputtered coatings of the same materials.

These results will be discussed in Section 4.

3.2. Alteration of T-U Curves

Figure 5 shows typical change of T-U curve due to the aging. The curve 1 corresponds to the freshly prepared sample (few days old), while the curve 2 corresponds to the sample stored over 400 days. Over this period of storage pretilt angle decays to zero or to the value which cannot be distinguished from zero by our measuring method. One can see that T-V curve becomes steeper. This might be caused by pretilt angle decay leading to threshold-like reorientation behavior. The second

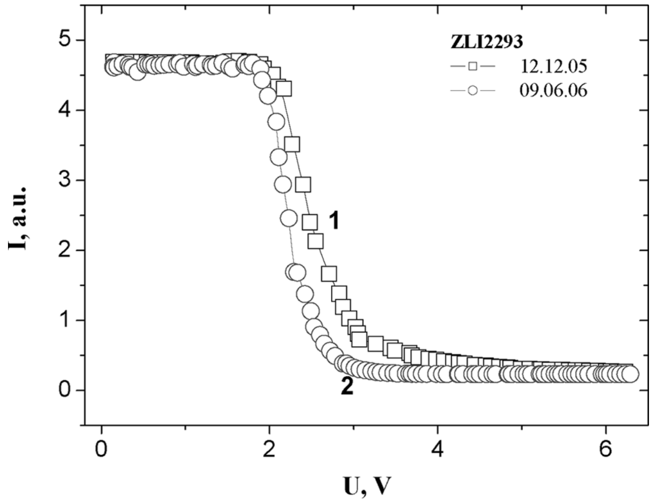

FIGURE 5 Transmittance vs. voltage curves for TN cell based on plasma beam processed PI 2555 substrates filled with LC ZLI2293: (1) two days after cell preparation; (2) 300 days after cell preparation.

feature is lowering of the controlling voltage. The latter might be explained by weakening of polar anchoring strength. It should be, however, experimentally proven. Noticeably, the cells with fully relaxed pretilt angle do not display alignment nucleation and appearance of defects when an electric field is applied. This might suggest that either the pretilt angle is not exactly zero (is zero just within measurement accuracy) or the alignment substrate memorizes the pretilted state determining rotation direction in an electric field.

4. DISCUSSION

Let us speculate now about aging mechanisms. According to [6], the alignment aging originates from the alteration of boundary layers caused by their reactivity. The action of accelerated ions results in a chain scission and formation of dangling bonds (free radicals) on the treated surface. In the interface layers these radicals react with LC causing change of boundary conditions and so alignment alteration. Within this model the decay of the anisotropy of bonds on the aligning surface is the main alignment factor.

We believe that the nature of alignment aging is more complicated and other factors may substantially influence the degradation process. One of them is a change of topology of alignment films under the ion/plasma beam exposure. Indeed, together with anisotropy of atomic bonds, the anisotropy of surface topology can be an important factor of LC alignment [15,16], also on the ion beam treated films [7]. Under the action of ions or plasma the topology can be substantially changed, because of appearance and agglomeration of low molecular weight surface species, melting and recrystallization of alignment film [17]. These processes soften the alignment film decreasing anisotropy of surface relief and thus alignment strength. The low molecular weight species may also provoke alignment degradation due to partial solution in LC. In parallel, the mentioned processes destroy anisotropy of surface atomic bonds that also leads to alignment deterioration. In general, surface chemical properties are interdependent with topological characteristics [18].

The other factors which may influence LC alignment, especially pretilt angle and polar anchoring energy, are surface charging and adsorption of atmospheric ions. The processing with the ion or plasma beam may cause substantial charging of the alignment layers. After removal from a vacuum these substrates attract ions from an air to compensate the introduced charge. The ions adsorb onto the alignment surface causing a kind of passivation. The desorption kinetic of these ions determines surface reactivity and so rate of LC-substrate reaction discussed above.

Our results suggest that manifestation of aging depends on the content of both liquid crystals and alignment films. Different ageing behavior for different LC implies various reaction stability of LC mixtures. The E7 mixture is most inert to surface reactions.

In the frame of our concept, one can readily explain different aging on different alignment substrates. The most intensive aging on synthetic polyimide can be caused by the effective scission of its linear chains with formation of low molecular weight species capable of agglomeration and partial solution in LC. The considerable change of surface topology by rinsing PI substrates in toluene [7] may be an indirect proof of this fraction. For the highly crosslinked plasma coatings the formation of low molecular weight species should be inefficient. This explains their improved aging resistance. Finally, faster alignment ageing for the sputtered films than for the PECVD films may be caused by a lower concentration of atomic links.

5. CONCLUSIONS

The phenomenon of alignment aging is studied for several types of liquid crystals and alignment materials considering pretilt angle degradation as a measure of this process. The degradation manifests itself in the decay or increase of pretilt angle depending on content of LC and alignment layer. The change of alignment leads to alteration of electro-optic characteristics and so image distortions in real LCD. The inorganic coatings obtained by PECVD method demonstrate the best aging resistance. This might be caused by high density of crosslinking which prevents formation of low molecular weight reactive species under the ion beam milling. The origin of such species is believed to be an important reason for alignment aging.

REFERENCES

[1] Little, M. J., Garvin, H. L., & Lee, Y. (1979). *US Patent* No 4,153,529.

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

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

[4] Yaroshchuk, O., Zakrevskyy, Yu., Dobrovolskyy, A., & Pavlov, S. (2001). *Asia Display/IDW'01*, 73.

[5] Wu, K. Y., Chen, C. H., Yeh, C. M., Hwan, J., Liu, P. C., Lee, C. Y., Chen, C. W., Wei, H. K., Kow, C. S., & Lee, C. D. (2005). *J. Appl. Phys.*, *98*, 083518-1.

[6] Katoh, Y., Nakagawa, Y., Odahara, S., & Samant, M. (2002). *US Patent* 2002/0063055 A1.

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

[8] Yaroshchuk, O. V., Liu, P. C., Lee, C. D., Lee, C. Y., Kravchuk, R. M., Dobrovolskyy, A. M., Protsenko, I. M., Goncharov, A. A., & Lavrentovich, O. D. (2005). *Proc. IMID'05*, 768 (Seoul, Korea, July 19–23).

[9] Yaroshchuk, O. V., Kravchuk, R. M., Dobrovolskyy, A. M., Protsenko, I. M., Goncharov, A. A., Liu, P. C., Lee, C. D., Lee, C. Y., Lavrentovich, O. D., & Muravski, A. *Proc. Eurodisplay '05*, 521 (Edinburgh, UK, Sept. 19–22, 2005).

[10] Nelson, J. (2003). *The Physics of Solar Cells*, Imperial College Press: London, UK.

[11] Khakhlou, A., Murauski, A., Yaroshchuk, O., Telesh, E., & Kravchuk, R. (2006). *J. SID.*, *14*(3), 257.

[12] Yaroshchuk, O., Kravchuk, R., Dolgov, L., Telesh, E., Khokhlov, A., Brill, J., Fruehauf, N., & Reijme, M. A. *Proc. of ADT'05*, 240 (Crimea, Oct., 2005).

[13] Yaroshchuk, O., Kravchuk, R., Dobrovolskyy, A., Klyui, N., & Korneta, O. *Proceeding of the XI-th Intern. Symposium "Advanced display technologies"*, 186 (Crimea, Ukraine, Sept. 8–12, 2002.)

[14] Kovalchuk, O., Zakrevska, S., Yaroshchuk, O., & Maschke, U. (2001). *Mol. Cryst. Liq. Cryst.*, *368*, 129.

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

[16] Barberi, R., Dozov, I., Giocondo, M., Iovane, M., Martinot-Lagarde, Ph., Stonescu, D., Tonchev, S., & Tsonev, L. (1998). *Eur. Phys. J. B*, *6*, 83.

[17] Overney, R. M., Gunherodt, H.-J., & Hild, S. J. (1994). *J. Appl. Phys.*, *75*, 1401.

[18] Greenwood, O. D., Hopkins, J., & Badyal, J. P. S. (1997). *Macromolecules*, *30*, 1091.