Polymer Films Treated with Plasma Beam as Aligning Substrates for Liquid Crystals

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ABSTRACT

The liquid crystal (LC) alignment on the polymer layers treated with a collimated beam of accelerated plasma is studied. Polyninylcinnamate (PVCN), a well-known photoaligning material, was chosen as an aligning polymer. 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. It is shown that azimuth anchoring energy on the plasma treated (PT) substrates is close to that one obtained for photoalignment (PA) method. At the same time, the generated pretilt angle is higher and more thermally stable on the plasma treated PVCN layers. A combined treatment with plasma and UV light is also considered as a method of LC alignment.

1. INTRODUCTION

In spite of many advantages compared with rubbing method, photoalignment technique is still not used for the mass production of LCD because of several principle technological problems. The major disadvantages of this technique (low anchoring energy, poor thermostability and pronounces image sticking) are well-known [1]. The most important reason of the mentioned drawbacks seems to be a quite soft treatment of the aligning substrates.

To overcome shortcomings of the conventional photoalignment method, M. Hazegava[2] suggested to use deep UV irradiation. One more radical solution was suggested by P. Chaudhari et.al. [3]. It consists of oblique irradiation of the aligning polymer substrates with a collimated ion beam. Since ionic bombardment causes substantial material deposition in the surface area, the aligning surface is essentially modified. This method provides excellent LC alignment on both organic [3] and non-organic [4] substrates.

Recently, we suggested a new irradiation procedure resulting in a high quality LC alignment and combining the advantages of deep UV and ion beam irradiation [5]. In these studies we applied plasma beam as an irradiation source. The plasma curing of the LC aligning substrates has been used before to provide polymerization [6], implant various atoms [7-9] or etch the substrates [8-9]. As result, LC anchoring was strongly modified. In the present research, we use *collimated* beam of plasma allowing us, in addition to curing possibilities mentioned above, controlling direction of the induced easy axis of LC alignment. We report now the improvements, which bring a new irradiation procedure for materials traditionally used for LC photoalignment. The alignment parameters for the substrates treated with plasma beam and UV light are compared. Additionally, combined irradiation with plasma and polarized UV light is considered as a possible method for LC alignment.

2. EXPERIMENRAL

2.1. Substrates

We used polyvinylcinnamate (PVCN) purchased from Aldrich to prepare liquid crystal (LC) aligning layers. The polymer was dissolved in chloroform at a concentration of 20 g/L and subsequently spin coated onto glass slabs. The thickness of the polymer films was about 200 nm. The films were kept at 100 ^oC over 1 h to provide complete removal of solvent.

2.2. Irradiation Procedures

To irradiate the layers, we used a plasma accelerator of ACDE type [6] in which ions are accelerated in crossed **E** and **H** fields immediately within the plasma. The substrates were irradiated in vacuum with a collimated beam of Ar-plasma directed obliquely at the polymer surface. Energy and current density of the plasma beam were varied within 500-1000 keV and 10-100 $\mu A/cm^2$, respectively. The incidence angle α determined as an angle between plane of the substrate and the beam direction was changed within 20^0 and 90^0. The time of irradiation was varied in the interval of 0.5-5.0 min.

A 250 W mercury lamp was used as a source of UV light for irradiation of the PVCN substrates. 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 (4 mW, 10 min) and then with non-polarized light (10 mW, 0.5 min). A Glan prism was used to polarize the UV light.

2.3. Cells

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 PT substrates. The cell gap was maintained with spacers of 5 μm in diameter. The cells were filled with nematic LC ZLI 4801-000 (T_c=96°C) by Merck.

The pretilt angle of LC alignment was measured in symmetrical cells using the crystal rotation technique [9]. The azimuthal anchoring energy was determined from the experimentally measured twist angle in the combined cells [10].

3. RESULTS AND DISCUSSION

3.1. Irradiation with plasma beam

The substrates prepared with plasma treatment (PT) exhibit high quality LC alignment (Fig.1). The easy axis of the LC lies in the incidence plane of the beam of plasma. The thermal stability of this alignment is rather high: keeping the samples at 110° C (~15° above T_c of LC) for 30 min and then cooling down to room temperature did not cause deterioration of LC alignment. This is in big contrast to the samples prepared using the PA method, where the same heating procedure causes many orientational defects. The results of the crystal rotation method show that the LC on PT substrate tilts towards the direction of irradiation. It is in agreement with the result obtained in [3] for the ion beam irradiation. The value of the pretilt angle does not change after the heating procedure described above.

The dependencies of pretilt angle θ versus incidence angles α for various irradiation times τ are shown in Fig.2. As can be seen, the pretilt angle monotonically grows when α changes from 15° to 70°. On the other hand, the pretilt angle θ at a fixed incidence angle of plasma beam α is a non-monotonic function of irradiation time τ.

The θ versus α curves were measured for various current density j (Fig.3). As one can see, pretilt angle non-monotonically changes with the increase of j. A non-monotonic behaviour also demonstrates the dependence of θ on ion energy E (Fig.4).

Fig.1. Combined cell containing 45^0 twisted LC layer viewed between a set of polarizers. Plasma treated area is black. Polarizer is parallel to the rubbing direction on the bottom substrate, whereas analyzer is perpendicular to the induced easy axis in the PT substrate.

From these results, the irradiation conditions for the desirable values of pretilt angle can be optimized. For instance, the maximal value of θ (θ= 3^0) was reached at E=600 V, j=20μA/cm^2 and τ=2 min. Our results show an important regularity; change of the current density several times causes a change of θ equal to that obtained when the exposure time is varied the same number of times. Thus, pretilt angle is unambiguously determined by a particle dose, P_N, which is the number of ions affecting the alignment film for the time of treatment. However, the same is not true for the dose of energy, P_E, which is the total energy of ions bombarded the alignment substrate. In other words, an increase of energy dose by an increase of particle concentration (or current density) is not equal to the increase of P_E caused by increasing particle energy. This fact can be explained assuming that an increase of particle energy leads to a deeper penetration of ions in the alignment film, whereas an increase of current density results in a more intensive surface curing essentially without increasing the curing depth. The dependence of the azimuth anchoring energy, W_a, on the incidence angle of plasma beam α is shown

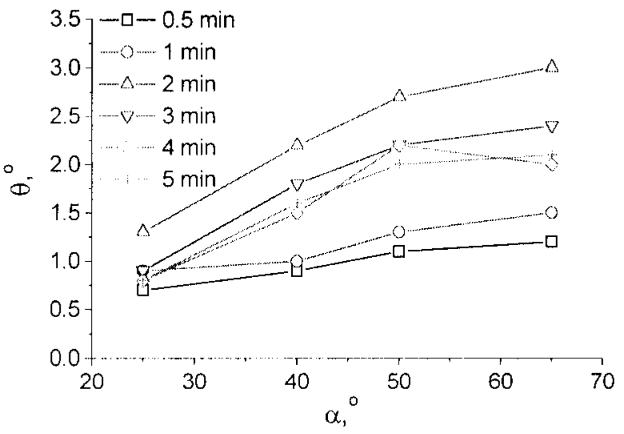

Fig. 2. Dependence of the LC pretilt angle θ on the incidence angle α of the plasma beam. E=600 V, j=20μA/cm^2. Dependencies are presented for various irradiation times.

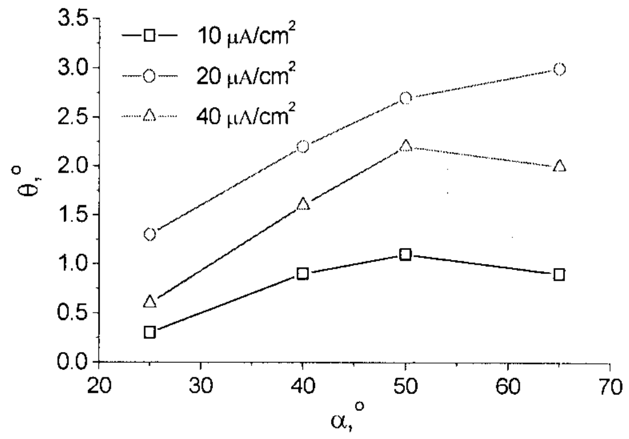

Fig. 3. The pretilt angle θ vs incidence angle α curves for three values of ion current density. Irradiation time is 2 min, E=600 V.

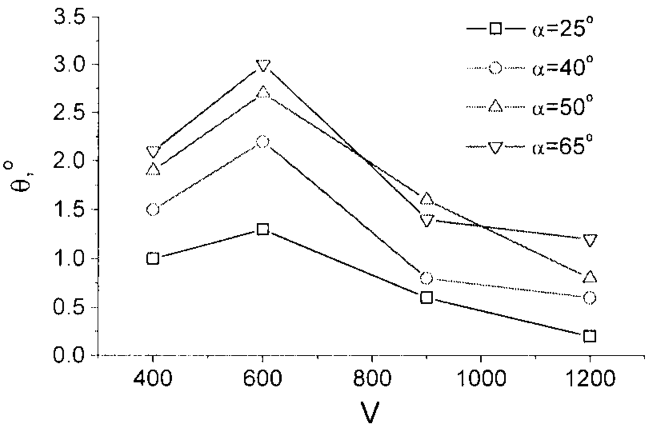

Fig. 4. The pretilt angle θ vs E curves for various values of beam incidence angle α. Irradiation time 2 min, j=20μA/cm^2.

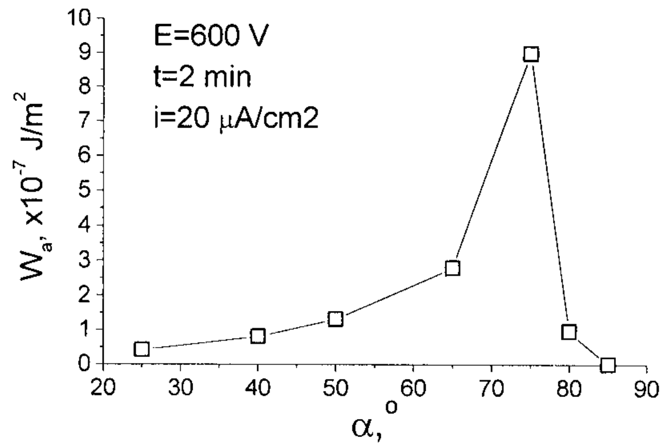

Fig. 5. Azimuthal anchoring energy of LC ZLI 4801-000 on PVCN substrates as a function of incidence angle α of the plasma beam.

in Fig. 5. The curve $W_a(\alpha)$ monotonically grows up to 75^0 then sharply decreases approaching zero. Simultaneously, the quality of LC alignment degrades. The abrupt decrease of the $W_a(\alpha)$ curve and deterioration of the LC alignment can be explained by assuming a low rate of surface anisotropy generated at the incidence angle α close to the film normal. Such azimuthal anchoring and, hence, quality of LC alignment decreases. As can be seen from the $W_a(\alpha)$ plot, maximal values of the azimuthal anchoring energy can be obtained at α=65-75^0. The energy is on the order of 10^{-6} J/m^{-2}, which is close to the value obtained for the photoirradiated PVCN substrate [8]. Note that at the same values of α, the highest values of the LC pretilt angle θ were obtained.

Investigations of the LC aligning mechanisms on PT substrates are under way. We detected that plasma treatment modifies the surface relief as well as the UV absorption spectra of PVCN layers. The detected spectral changes are similar to that for UV light irradiation. These results may reflect influence of both ion implantation and deep UV irradiation of plasma on LC alignment. Consequently, both the anisotropy of surface relief and the anisotropic distribution of polymer chains should be considered as possible alignment factors.

3.2. Combined irradiation with plasma and polarized UV light

Since both plasma beam and UV light can induce surface anisotropy in the PVCN film, we tried to compare various cases of irradiation including combined irradiation with both sources. In all cases of irradiation, a high quality LC alignment was observed. At the same time, the estimated values of pretilt angle strongly depended on the irradiation conditions. Substrates irradiated by the plasma beam provided a pretilt angle (~3^0) that is 3 times higher than substrates cured by UV light (~1^0). The ion irradiation of PVCN substrates preliminarily cured with UV light provides an increase of LC pretilt angle from 1^0 to 3^0. To the contrary, UV light irradiation following the procedure of PT leads to an effective suppression of θ. We believe that UV light action causes a smoothing of the surface relief, which should determine the value of pretilt angle.

4. CONCLUSION

Thus, oblique irradiation of the aligning substrates with a collimated beam of accelerated plasma is an effective method of LC alignment compatible with the photoalignment technique. It provides high quality LC alignment with a smooth control of pretilt angle and anchoring energy. The maximal values of azimuth anchoring energy generated by the PT technique are close to that for PA method. At the same time, the PT method provides several important advantages. LC pretilt on the plasma treated substrate is several times higher then on the UV irradiated aligning film. The alignment produced with PT method is substantially thermally stable in both azimuth and polar direction. Compared with photoalignment, the plasma irradiation is more general method, since it can be used to provide LC alignment on the non-photosensitive substrates. We observed LC alignment on the PT polymethacrylate and polystyrene layers, and even on the PT bare glass slabs. In the case of photosensitive polymers, PA and photoalignment methods can be combined. For instance, oblique irradiation with an ionic beam can be effectively used to remove double generation of LC pretilt on the photocured substrate and to increase the value of pretilt angle.

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