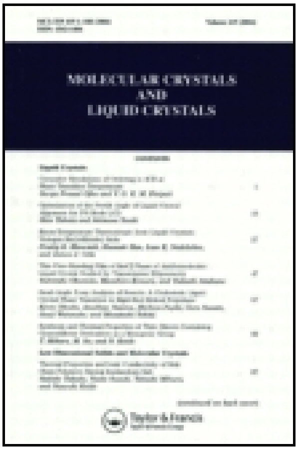

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Surface Alignment with High Pretilt Angle Using the Photoreactive Fluorinated Polymer Films

Hsin-Ying Wu [a], Chih-Yu Wang [a], Chia-Jen Lin [a], Ru-Pin Pan [a], Song-Shiang Lin [b], Chein-Dhau Lee [b] & Chwung-Shan Kou [c]

[a] Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan, Republic of China

[b] Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan, Republic of China

[c] Department of Physics, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

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Surface Alignment with High Pretilt Angle Using the Photoreactive Fluorinated Polymer Films

Hsin-Ying Wu[1], Chih-Yu Wang[1], Chia-Jen Lin[1]
Ru-Pin Pan[1], Song-Shiang Lin[2], Chein-Dhau Lee[2], and
Chwung-Shan Kou[3]
[1]Department of Electrophysics, National Chiao Tung University,
Hsinchu, Taiwan, Republic of China
[2]Material and Chemical Research Laboratories, Industrial Technology
Research Institute, Hsinchu, Taiwan, Republic of China
[3]Department of Physics, National Tsing Hua University, Hsinchu,
Taiwan, Republic of China

A newly developed fluorinated polymer film for liquid crystal alignment by applying ultra-violet (UV) irradiation or ion beam treatment is studied in this work. The surface alignment with high pretilt angle is achieved by the UV treatment. The induced pretilt angle by ion beam treatment on this photo-reactive polymer film, however, is relatively small. Surface analyses by x-ray photoemission spectroscopy and contact angle measurement are carried out to deduce the underlying mechanism. The result shows that the higher content of the fluorinated side-chain in polymer contribute to the lower surface energy and the higher pretilt angle. The atomic ratio of fluorine is largely decreased by ion beam treatments. The alignment uniformity and stability of the surfaces treated by linearly-polarized UV light and ion beam bombardment are also demonstrated.

Keywords: fluorinated polymer films; ion beam; nematic liquid crystals; pretilt angle; surface alignments; ultraviolet irradiation

I. INTRODUCTION

The applications of liquid crystal (LC) in optical devices have been widely investigated for decades. Especially in the area of information

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Address correspondence to Ru-Pin Pan, Department of Electrophysics, National Chiao Tung University, 1001 Ta Hsueh Rd., Hsinchu 30010, Taiwan. E-mail: rpchao@mail.nctu.edu.tw display, liquid crystals have received considerable attention due to its promising electro-optical properties. Furthermore, surface alignments of liquid crystals are essential in liquid crystal displays (LCDs). It determines the boundary condition for the molecular orientation at the surface. Currently, the mechanical rubbing is the most conventional method of surface alignment due to its low cost and reliable alignment ability. As a polymer with convincing thermal and mechanical properties, the polyimide (PI) is so far the most favorable alignment material in the conventional rubbing method owing to its high transparency, superior adhesion and chemical stability [1]. However, the mechanical rubbing method which employs a velvet rubbing process on the PI-coated substrates has some drawbacks such as leaving debris and electrostatic charges on the rubbed surfaces. Also, it becomes increasingly difficult to maintain uniformity as the substrate size of LCD gets larger rapidly in industry. Multi-domain or high pretilt angle alignment cannot be easily achieved either. Alternatively, contact-free alignment methods such as the photo-alignment [2–13], oblique evaporation [14–17] and ion-beam alignment [18–21] techniques have been vastly investigated to overcome the mentioned shortcomings. Intense studies have also been carried out to develop the alignment materials suitable for each alternative method. During the last decade, the photoreactive polymers have been extensively studied as the photoalignment layer including photo-decomposable polymers [4–7], photocrosslinkable polymers [2,8–10], and photo-isomerizable polymers [11–13]. Especially, the photoreaction of the PI has received considerable attention because of its being widely used in LCDs industries already [4,7,13]. However, long exposure time or high dosage of UV irradiation is required to achieve significant effect of surface alignment due to the low photoreactive efficiency of PI.

In this study, we demonstrate the alignment properties of nematic liquid crystal (NLC) on a fluorinated polymer film S46-F8 [22,23] treated by two different noncontact methods using the linearly polarized UV light (LPUVL) irradiation and argon ion beams (IB) bombardment. This material is developed jointly by the Syromyatnikov's group from Taras Shevchenko Kyiv National University of Ukraine, Yaroshchuk's group from Institute of Physics of NASU of Ukraine, and Lee's group from the Industrial Technology Research Institute, Taiwan. The surface-sensitive x-ray photoemission spectroscopy (XPS) studies have been carried out to evaluate the chemical compositions of the film surfaces. Furthermore, the surface energies of the treated films measured by using contact angle method are compared with the results from XPS analyses to find out the underlying mechanism.

II. EXPERIMENTS

The indium-tin-oxide coated glasses with size of 20 mm × 10 mm are used as the substrates. After cleaning process, the substrates are spin coated with the fluorinated polymer S46-F8, whose structure is shown in Figure 1. The spin rate is 500 rpm for the first 5 seconds and 2000 rpm for the 20 seconds afterward. The substrates are then pre-baked at 90°C for 10 minutes and cured at 150°C for another half hour. The integers, m and n, in Figure 1 indicate the degree of polymerization of the S46 block and F8 block, respectively. In this work, three S46-F8 polymer films with different values of n/m including 0, 1, and 2 are studied and labeled as F0, F1, and F2, respectively.

After the thermal treatment, the copolymer films are then treated by the LPUVL irradiations and IB bombardments separately. The LPUVL is obtained from a 1000 W Xenon arc lamp (Model 6269 Oriel) through a liquid filter, a convex lens and a Glan-Taylor prism in sequence. The schematic view of the setup is shown in Figure 2. The liquid filter is designed to absorb the infrared radiation lying below the red end of visible spectrum. The intensity of the LPUVL irradiation is enhanced by focusing the light beam on the sample area using the convex lens. The output intensity of the broadband irradiation at the position in which the samples are set is measured to be 3 mW/cm^2. The photo-induced alignment is accomplished with a two-step irradiation process, which includes a LPUVL exposure at first and then an unpolarized UV light exposure with intensity of

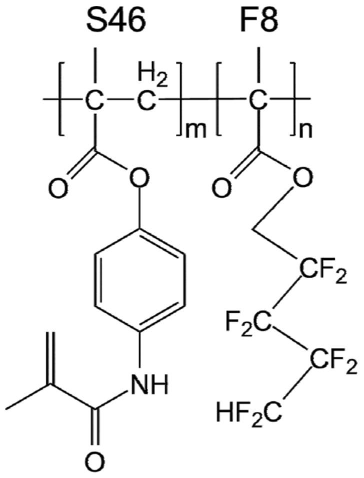


FIGURE 1 The chemical structure of the fluorinated polymer S46-F8.

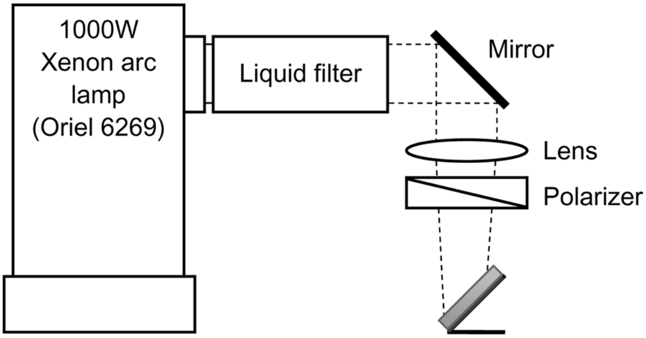


FIGURE 2 Schematic diagram of the LPUVL irradiation system.

12 mW/cm^2 for another 1 min to remove the degeneracy of the pretilt angle. The incidence angle of UV light is 45° throughout the process.

In this study, a diode sputter (model IB-2 from EIKO Engineering Co., Ltd.) has also been used for the IB treatment on polymer surface to compare the alignment properties and to deduce the mechanisms. The details of our IB treatment have been already described in the previous work [24,25]. The etching mode is selected in this work. The parameters of IB treatment such as the incidence angle, the current density and the direct-current bias between the electrodes are fixed at 60°, 255 μA/cm^2, and 420 V, respectively.

For the alignment characterization, two equally treated substrates are assembled with a 23 μm Mylar spacer in between with anti-parallel alignment direction to form an empty cell. The nematic liquid crystal (NLC) 4′-n-pentyl-4-cyanobiphenyl (5CB, Merck) with a nematic range between 24.0°C and 35.3°C is then filled into the empty cell.

The alignment qualities of the LC cells are characterized by looking with a pair of crossed polarizers. The pretilt angle of 5CB molecules near the surface is measured by using the "crystal rotation method" [26]. To clarify the relation between the surface energy and the induced alignment properties of the treated films, the contact angle measurements have also been carried out. The polar, dispersive, and total surface energy are evaluated according to the Owens-Wendt method [27]. In this method, the surface energy of a solid γ_s can be resolved into a dispersion and a polar component denoted as γ_s^d and γ_s^p, respectively, by

$$1 - \cos\theta = \frac{2}{\gamma_l}\left(\sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p}\right),$$

where θ is the contact angle, γ_l is the surface tension of the liquid which is in contact with the solid surface, $\gamma_l = \gamma_l^d + \gamma_l^p$ and $\gamma_s = \gamma_s^d + \gamma_s^p$. Two liquids, water and glycerol, are used in the contact angle measurements and their surface energies, $\gamma_{water}^d = 21.8\,\mathrm{mJ/m^2}$, $\gamma_{water}^p = 51.0\,\mathrm{mJ/m^2}$, $\gamma_{glycerol}^d = 37.0\,\mathrm{mJ/m^2}$, $\gamma_{glycerol}^p = 26.4\,\mathrm{mJ/m^2}$ are obtained from the literature [28].

Furthermore, XPS studies have been carried out to analyze the compositions of chemical bonds of the surface-treated S46-F8 film. With sputter etching using the equipped ion gun in the XPS system (PHI-1600), the quantitative element compositions in various depths are determined. For the XPS, a dual-anode x-ray monochromatic source for the x-ray irradiation of Mg Kα (1253.6 eV) and Al Kα (1486.6 eV) and a PHI 10-360 precision energy analyzer are used. The incident angle of the x-ray is 36° from the sample normal and the photoelectrons are detected at the angle of 45° from the sample normal. The base pressure during acquirement is below 5.0×10^{-9} Torr. The anode voltage is set at 15 kV (x-ray power 250 W).

III. RESULTS AND DISCUSSION

After annealing of the LC cells, the surface alignment of each cell is examined with the crossed polarizers. Figure 3 shows the photographs of the LC cells with F0, F1, and F2 films treated by LPUVL irradiations and IB bombardments for 10 min. Both treatments on this copolymer film can give significant alignment effects. It is clarified that the alignment directions of each LC sample are parallel to the incidence plane of IB or perpendicular to the polarization of UV light. However, more defects exist on the UV-treated surfaces. The amount seems to be related to the quantities of fluorinated monomer F8. The measured pretilt angles are shown in Figure 4. Remarkably, the highest pretilt angle induced by IB treatment is still much smaller than that induced by the LPUVL-irradiated surfaces. The pretilt angle also increases with the fluorine content of polymer film. The results also show that the largest pretilt angle is achieved in about 5 min for both alignment methods. Longer treatment time will reduce the pretilt angle. The error bar in Figure 4 is obtained by averaging the measured values over different positions on the surface.

In the XPS studies for the treated films, we first survey scan over all the spectrum range with a step size of 1 eV and analyzer pass energy of 117.4 eV. The analysis for each involved element reveals that the fluorine content on the IB-treated surface is dramatically decreased no matter how short the treatment takes. The reaction between

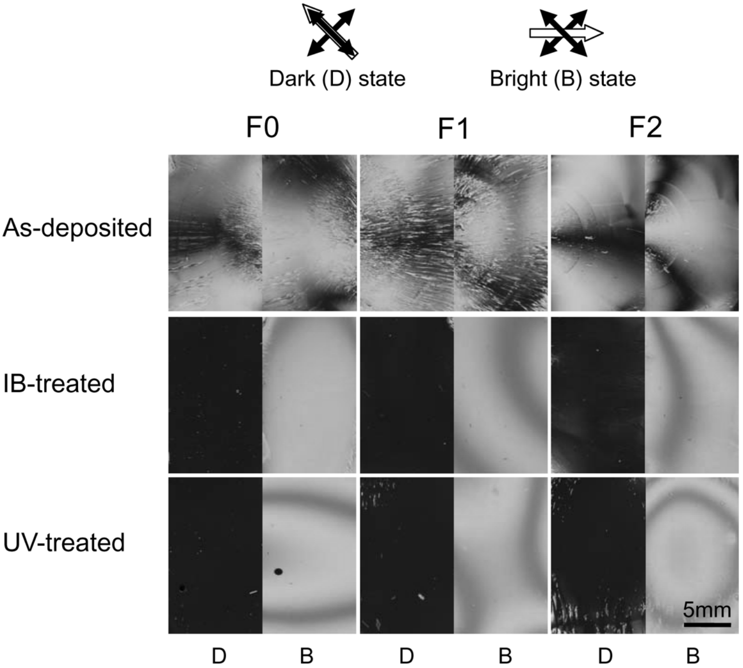


FIGURE 3 The photographs of 5CB cells under crossed polarizers. The cells are aligned with surface-treated F0, F1, and F2 films by LPUVL irradiation and IB bombardment for 10 min.

oxygen and dangling bond induced by ion beam bombardment causes the significant increasing to oxygen content. However, no apparent change in the content of fluorine and oxygen is found on the LPUVL-irradiated surface. For the F2 polymer film, the further scan with multiplex mode about C_{1s} and F_{1s} peaks are accomplished with a step size of 0.2 eV and analyzer pass energy of 46.95 eV, as shown in Figure 5. Notice that the intensity of the peak at 290.9 eV corresponding to the CF_2 bond decreases after surface treatments. Figure 5(a) shows that the significant reduction of intensity is not observed until the LPUVL treatment last over 10 min (2.52 J/cm^2). Contrarily, the grafted fluorinated groups in the F8 monomer are mostly destroyed in the IB treatment even though the treatment duration is only 2 min, as shown in Figure 5(b). The same behavior is also found in the F_{1s} spectrum, as shown in Figure 5(c). The contribution of CF bond at 687.6 eV to the overall signal becomes significant for 10 min LPUVL treatment.

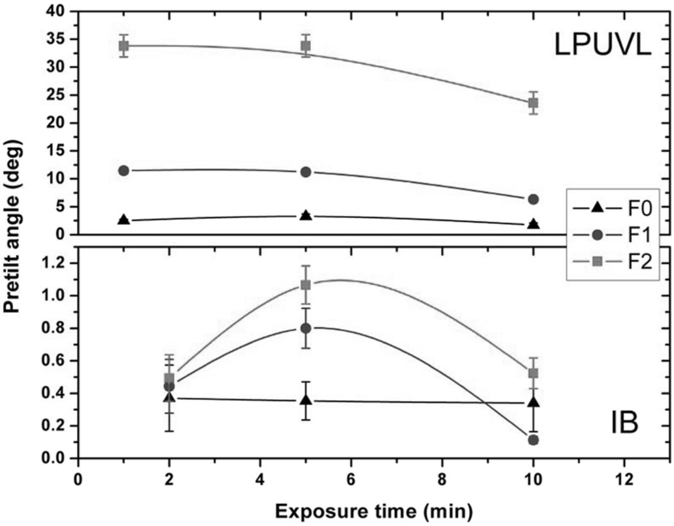
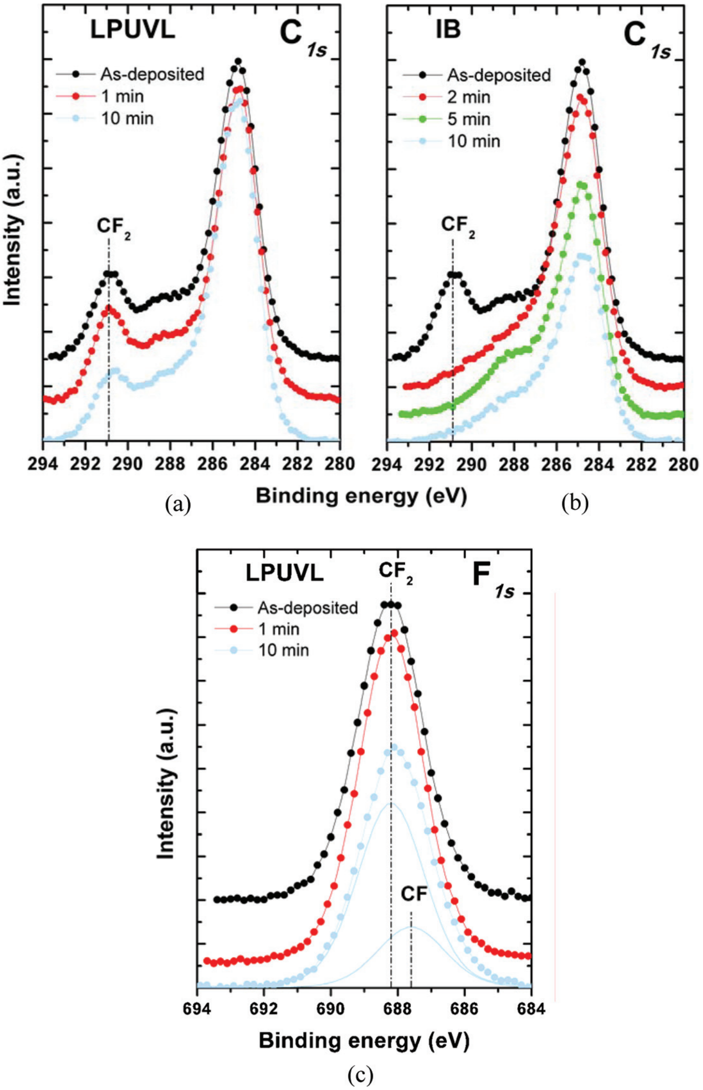


FIGURE 4 The pretilt angle as a function of the exposure time for different S46-F8 films treated by both alignment methods.

As described in the literature, the incorporation of fluorine in a polymer film generally causes the polymer to have a lower surface energy [29]. The results of our surface energy measurement are plotted against the exposure time as shown in Figure 6. Without the surface treatments, the surface energies of F0, F1, and F2 polymer films are given as 45.4, 33.1, and 29.1 mJ/m^2, respectively. As expected, a lower surface energy corresponding to a higher pretilt angle is owing to a higher content of fluorinated fragment in a polymer film. After surface treatments, an apparent increase of the surface energy is found for the IB-treated films, while it is unchanged for the LPUVL-treated films. These results also suggest that the IB treatment reduces the fluorine content in the films. It is also worth to notice that no significant anisotropy of surface energy is found in our samples treated by either method.

It is known that the LC alignment mode is ascribed to the competition between the surface tension of solid surface γ_s and LC molecules γ_{LC} mentioned in Creagh *et al.*'s work [30]. They concluded that a homeotropic alignment of LC is obtained if $\gamma_{LC} > \gamma_s$, otherwise, a homogeneous alignment occurs. Even though this conception is suitable for our case, this model is not absolutely correct without exceptions demonstrated by Uchida *et al.* [31].



(a) (b)

(c)

FIGURE 5 XPS spectra for F2 films treated by both noncontact methods with different exposure times. The C_{1s} spectra for (a) LPUVL-irradiated films and (b) IB bombarded films and (c) the F_{1s} spectrum for LPUVL-irradiated films.

Furthermore, depth analyses of XPS have also been accomplished for 10 min LPUVL-treated and as-deposited F2 films as shown in Figure 7. The measured atomic ratio for C, O, N, and F are 41.5,

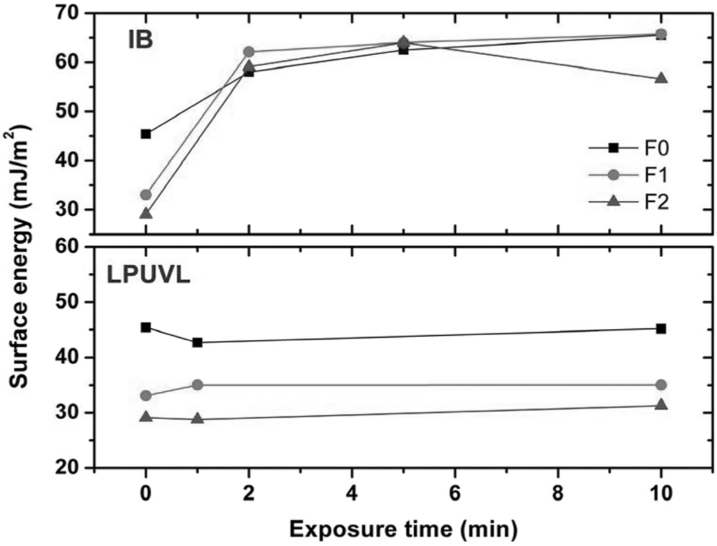


FIGURE 6 The surface energy as a function of the exposure time for different S46-F8 films treated by both alignment methods.

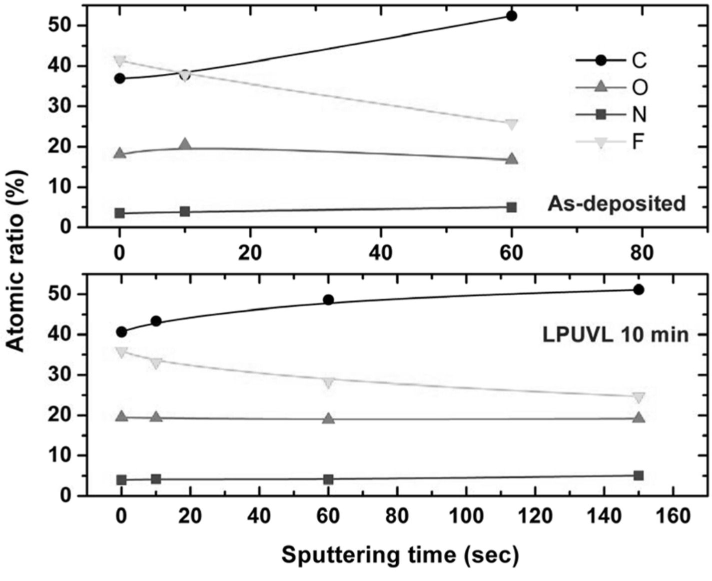


FIGURE 7 The depth-dependencies of C, O, N, and F content in the as-deposited and LPUVL-irradiated F2 films.

18.1, 3.5, and 36.9%, respectively, for an as-deposited F2 film. However, compare with the calculated values, more fluorine content about 8.8% is found on the surface. It reveals that the fluorine side chains predominantly move to the film surface.

IV. CONCLUSION

The alignments properties and the mechanism related to high pretilt angle of a newly developed fluorinated polymer film S46-F8 treated by LPUVL irradiation and IB bombardment are demonstrated in this work. A saturated pretilt angle about 34° is achieved on the LPUVL-irradiated F2 film surface with dosage of $0.9\,\mathrm{J/cm^2}$. The photodecomposition becomes significant in the LPUVL treatments with dosage approximately higher than $1.6\,\mathrm{J/cm^2}$. The ion beam treatment reduces both fluorine content and the pretilt angle drastically. We conclude that the content of fluorinated groups CF_2 grafted in the F8 side chains plays a dominant role while determining the pretilt angle. No remarkable anisotropy of surface energy is found on the surfaces treated by both methods. It is also observed that the fluorinated side chains are preferentially clustered at the surfaces.

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