# Investigation of the alignment layers on fluorinated amorphous carbon films by plasma beam aligning

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**Abstract:** The liquid crystal alignment of fluorinated carbon films which deposited on the ITO glass has been improved by plasma beam aligning. The a-C:F films properties and LC cell measurement were estimated to investigate the relationship between the gaseous $H_2$/Ar ratio and LC alignment characteristics. It was found that the ion bombardment of films have a minimal impact on the alignment properties. Moreover, the $H_2$/Ar plasma beam aligning induces bond-breaking and chain scission from the XPS results. Finally, the F/C ratio of a-C:F films could be controlled by the $H_2$/Ar ratio and it could indicated the pretilt angle.

**Keywords:** a-C:F films, plasma beam aligning, pretilt angle, F/C ratio.

## 1. Introduction

The alignment layers play an important role for liquid crystal display (LCD), and the alignment technology has been used to align liquid crystal (LC) molecules along a certain direction. Until now, a rubbing technology has been used to align LC molecules on polyimide (PI) films [1]. The rubbing method generates parallel grooves of micron size. The grooves are useful for the enhancement of LC alignment, which was called grooving mechanism [2]. However, for the current generation of rubbing technology, the mechanical rubbing method has some drawbacks, such as the surface electrostatic charges, broken debris, alignment irregularity, and contaminating particles [3]. To avoid these drawbacks, some non-contact alignment technologies such as ultraviolet (UV) light irradiation [4], Kaufman ion beam alignment [5], and plasma beam alignment have been developed [6]. The non-contact alignment methods were expected to replace the mechanism rubbing method. Until now, PI films and diamond-like carbon (DLC) films were used for alignment layers. Recently, a plasma beam alignment has been developed to enhance the properties of LC alignment for PI and DLC films [7]. The different properties (associated with plasma beam alignment and Kaufman ion beam alignment) were that plasma beam alignment requires no extra electric field to extract ions and the plasma-beam flux is generated by anode layer thruster (ALT) [8].

The amorphous fluorinated carbon (a-C:F) films have attracted the attentions of researchers and practitioners alike due to their chemical stability, low surface energy, low refraction, good electrical and thermal properties. The unique property of a-C:F films is hydrophobic surface to compare with DLC films. The precursors for depositing a-C:F films include fluorine containing compounds and hydrogen containing additives [9].

In the present study, the physical and chemical properties of a-C:F films by $H_2$/Ar plasma beam aligning were investigated. In the meantime, a-C:F films properties and LC cell measurement were used to investigate the relationship between the gaseous $H_2$/Ar ratio and LC alignment. The relationship between the fluorine-to-carbon (F/C) ratios and pretilt angle has found to have a major impact on the formation of the a-C:F films.

## 2. Experimental Procedures

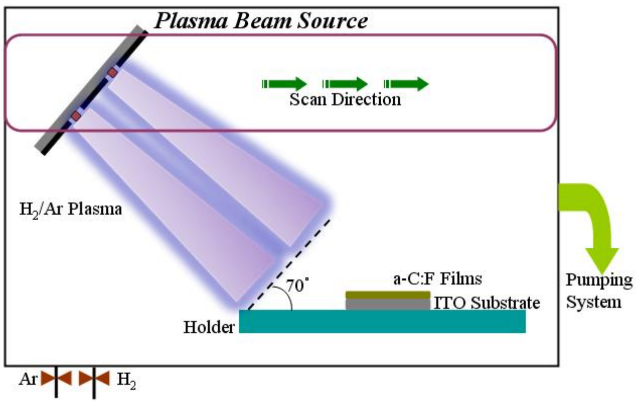



Fig. 1 Schematic diagram of a plasma beam aligning system.

The a-C:F films were deposited on substrates such as 30 cm-Ω indium tin oxide (ITO) glasses and single crystalline silicon in a plasma-enhanced chemical vapor deposition (PECVD) reactor. During the preparation process, all substrates were cleaned ultrasonically prior to depositing a-C:F films. In addition, all substrates were cleaned with acetone and de-ionized (DI) water. The pre-depositing substrates were cleaned for 1 min in $O_2$ plasma. Subsequently, the a-C:F films were deposited in a quartz bell jar reactor with an external electrode for radio-frequency (RF) power. The a-C:F films were deposited by $C_6F_6$ plasma at 100 W of radio-frequency (RF) power and a working pressure of 300 mtorr. The depositing time was 1 min to obtain a uniform a-C:F films. The thicknesses of a-C:F films were about 140-150 nm. The chemical composition such as the F/C ratio and C-$F_x$ bonding structure of a-C:F films were measured by X-ray photoemission spectroscopy (XPS).

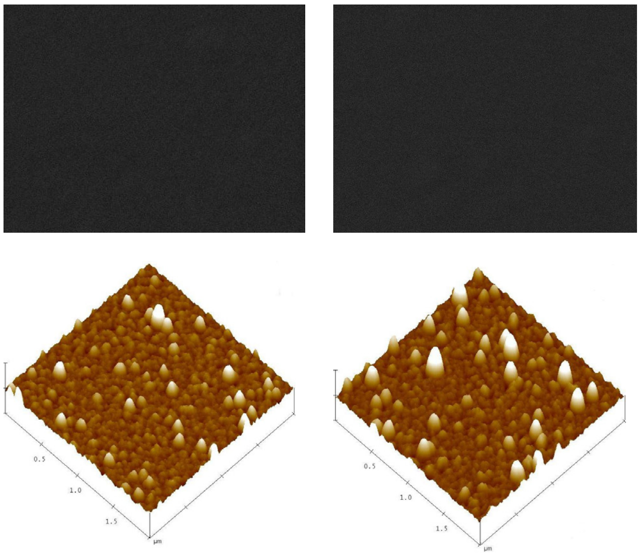
The $H_2$/Ar plasma beam aligning was used for the treatment of a-C:F films. Figure 1 shows the schematic diagram of a plasma beam aligning system. The plasma characteristics are controlled by the process parameters. In the process experiment, the applied voltage of a plasma beam aligning was 400V at a working pressure of 1.2 mtorr. The incident angle of a plasma beam aligning was fixed at 20° with the scanning speed of 6 mm/s. The distance between the a-C:F sample and the plasma beam source was set to be 60 mm. The gaseous $H_2$/Ar ratio (ranging from 0% to 100%) was the key factor determining the outcome of the plasma beam aligning. Subsequent to the plasma beam aligning, the physical characteristics of a-C:F films were measured by scanning electron microscope (SEM) and atomic force microscopy (AFM), which the hydrophobic characteristic was measured by contact angle analyzer (CAA).

The twisted nematic (TN) LC cells of 20 mm×30 mm were assembled using the an anti-parallel configuration. The pretilt angle of TN LC cells was measured by crystal rotation method. The type of a TN LC was ZLI-2293, and the gap of the LC cell was about 30 μm. Finally, the LC alignment ability was measured by polar optical microscope (POM).

## 3. Result and Discussion

### *3.1 Ion bombardment reaction*

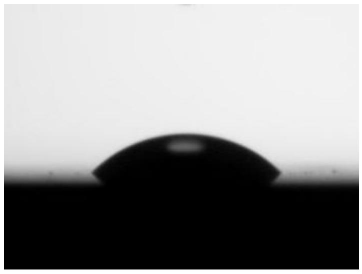
From the ion bombardment view point, Fig.2 shows the morphology (SEM & AFM images) of a-C:F films by $H_2$/Ar plasma beam aligning. It was known that surface treatments made by plasma could result in both surface cross-linking and chain scission. For this study, as observed by SEM, the surface variation of a-C:F films resulting from plasma beam aligning has a minimal effect. The roughness (expressed in terms of its root-mean-square value, Rms) of a-C:F films was measured to be below 5 nm before and after the alignment. No obvious surface grooves of a-C:F films were observed after plasma beam aligning. As a result, the ion bombardment has a minimal impact on the surface morphology.



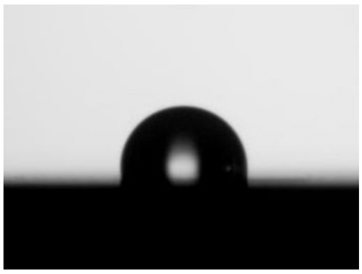
(a) (b)

Fig. 2 SEM & AFM images of a-C:F films: (a) aligned with gaseous $H_2$/Ar = 1; (b) non-aligned.

### *3.2 Chemical reaction*



(a)



(b)

Fig. 3 Contact angle images of a-C:F films: (a) aligned with gaseous $H_2$/Ar = 1; (b) non-aligned.

The contact angle images of a-C:F films were measured before and after the $H_2$/Ar plasma beam aligning, as shown in Fig. 3. A significant decrease in the contact angle was observed after $H_2$/Ar plasma beam aligning. The contact angle of a-C:F films was 103.5° and 45.3°, respectively, before and after $H_2$/Ar plasma beam aligning. The surface property of a-C:F films was hydrophobic without alignment. The F concentration of a-C:F films decreases substantially by $H_2$/Ar plasma beam aligning, due to the fact that the scission of C-F bonds was measured by $H_2$/Ar plasma beam aligning. From the result shown in Fig. 3, the hydrophobic property of a-C:F films reduces significantly by $H_2$/Ar plasma beam aligning.

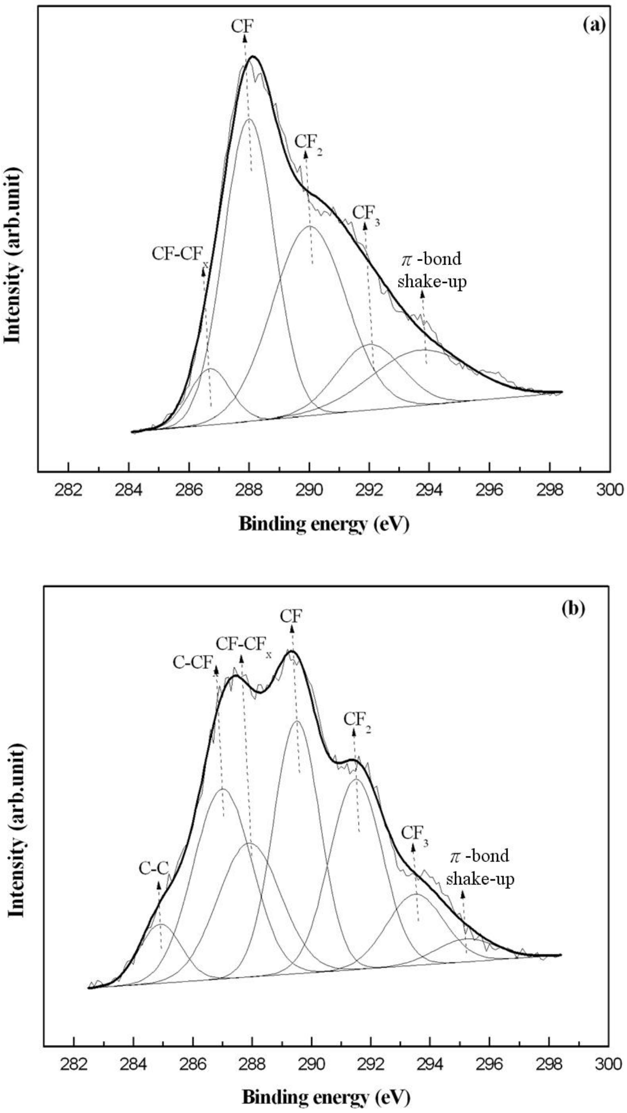
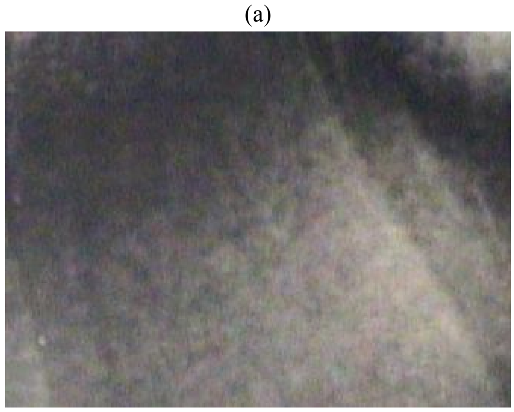



Fig. 4 C 1s spectra of a-C:F films as a function of F concentration: (a) aligned with gaseous $H_2$/Ar = 1; (b) non-aligned.

To investigate the surface chemical bonds of a-C:F films for a $H_2$/Ar plasma beam aligning, XPS was used for measurements. Fig. 4 shows the C 1s spectra of a-C:F films as a function of F concentration, measured by XPS. It is noted that XPS can detect the F concentration as well as the cross-linking in the a-C:F films. The measurements show relative magnitudes of F and C before and after the $H_2$/Ar plasma beam aligning. The deconvolution of C 1s XPS spectra shows the various $CF_x$ groups in a-C:F films. According to Yang and Oh [10], the peaks at 284.6, 286.4, 287.9, 289.2, 291.2, 293.2 and 294.9eV were assigned to C-C, C-$CF_x$, CF-$CF_x$, CF, $CF_2$, $CF_3$ and $\pi$-bond shake-up, respectively. The main features of C 1s XPS spectra include C-$CF_x$, CF, CF-$CF_x$, $CF_2$ and $CF_3$ compositions a-C:F films. It was found that the intensities of the $CF_2$ and $CF_3$ species decrease, while that of C-$CF_x$ increases after $H_2$/Ar plasma beam aligning. According to previous study, carbon network preferred to combine with $CF_2$ and $CF_3$ bonds with an increase of the F concentration in a-C:F films. The $CF_2$ and $CF_3$ bonds were basic units of polytetrafluoroethylene (PTFE) and as a result of this, the surface is hydrophobic [11]. From the results shown in Fig. 4, it is observed that the amount of $CF_2$ and $CF_3$ bonds decreases substantially by $H_2$/Ar plasma beam aligning, since the C-F bonds were destroyed by $Ar^+$ and H radical in a-C:F films. This clearly shows that the hydrophobic property of a-C:F films decreases by $H_2$/Ar plasma beam aligning.

### *3.3 TN LC cells measured*

(a)



(b)

Fig. 5 POM photographs of TN LC cells. (a) aligned with gaseous $H_2$/Ar = 1; (b) non-aligned.

The photographs of TN LC cells, obtained by polar optical microscope, were taken before and after the $H_2$/Ar plasma beam aligning, as shown in Fig. 5. The LC alignment effect is preferable with a-C:F films treated by various gaseous $H_2$/Ar ratio (ranging from 0% to 100%) of plasma beam. As shown in Fig. 5, the experimental results indicate that an excellent uniformity in a-C:F alignment films was attained by using the $H_2$/Ar plasma beam aligning.

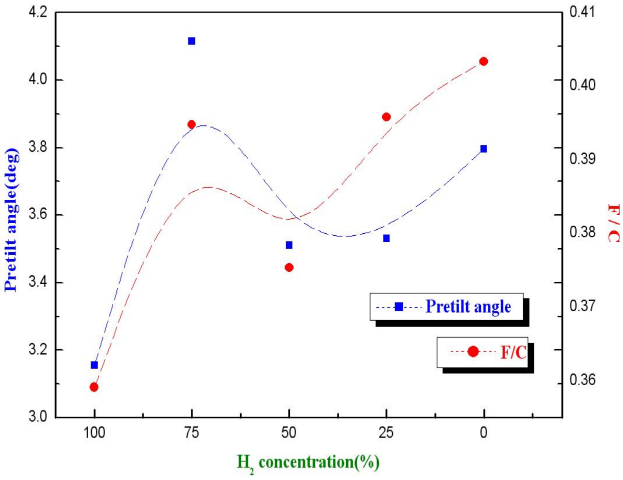



Fig. 6 The pretilt angle and F/C ratio on a-C:F films as a function of $H_2$/Ar ratio.

In order to understand the impact of treatment of $H_2$/Ar plasma beam aligning on the LC alignment, a crystal rotation method was used to measure pretilt angle by various gaseous $H_2$/Ar ratios. It is noted that the pretilt angle of non-alignment is close to 0°. The pretilt angle of a-C:F films are about 3.15 – 4.11° with various gas $H_2$/Ar ratios. The pretilt angle and F/C ratio on a-C:F films as a function of $H_2$/Ar ratio are shown in Fig. 6. When the volumetric flow rate of $H_2$ is greater than that of Ar, $H_2$ will be dissociated to generate radicals, enhancing the chemical etching reaction on the a-C:F films, as shown in Fig. 6. Since the dissociation rate of $H_2$/Ar is low, the amount of fluorine being changed by the dissociated $H_2$/Ar is low as well, leading to a low quantity of fluorine being carried away by the $H_2$ stream. On the other hand, as the flow rate of Ar increases, the overall dissociation rate of $H_2$/Ar is also increased, resulting in a more effective ion bombardment. In the meantime, the dissociated ion, $Ar^+$, breaks the bonding of the a-C:F films, leading to a reduction the amount of fluorine at the film surface. As the ratio of $H_2$/Ar becomes unity, the dual effect of chemical etching reaction and ion bombardment causes a drastic reduction in the amount of fluorine. From the curve of pretilt angle as shown in Fig. 6, it is observed that this curve follows the trend of the F/C ratio curve. It should be noted that the amount of fluorine on the film surface has a major effect on the hydrophobia property of the surface. It should also be that Fig. 6 provides the graphs for the relationship between $CF_2$ and $CF_3$ bonds and the pretilt angles.

## 4. Conclusion

An effective methodology of determining the relationship between the films' F/C ratio and pretilt angle has been proposed in this paper. The LC alignment quality of a-C:F films deposited on the ITO glass was observed to be improved by plasma beam aligning. Besides, the ion bombardment of a-C:F films was found to have a minimal impact on the alignment characteristics. From the experimental results as observed by XPS, the $H_2$/Ar plasma beam aligning induces bond-breaking and chain scission of the a-C:F films. The $CF_2$ and $CF_3$ bonds play an important role of hydrophobic property with various $H_2$/Ar plasma beam aligning. Finally, it was observed that the F/C ratio of a-C:F films is controlled by the $H_2$/Ar ratio.

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