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Liquid crystal alignment on the a-C:H films by Ar plasma ion immersion

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Abstract

A plasma ion immersion treatment has been developed to enhance the liquid crystal (LC) alignment on the hydrogenated amorphous carbon (a-C:H) layer in an inductively coupled plasma (ICP) chamber. No LC alignment was observed for the a-C:H layer tilted at an angle of 0° during the bombardment with plasma ions. The LC alignment occurs for the a-C:H layer tilted at an angle of 30° or 60°. Their pretilt angles ($\sim 1.4°$) are approximately the same. The azimuthal anchoring strength is 1.98×10^{-6} J/m^2 at a tilted angle of 30° and 1.14×10^{-4} J/m^2 at a tilted angle of 60°. The mechanism for the LC alignment is attributed to the oblique incidence of ions within the matrix sheath of non-uniform thickness near the a-C:H surface under a negative pulse bias. The matrix sheath of non-uniform thickness is confirmed by the plasma density distribution in the ICP chamber and the X-ray photoemission spectra across the a-C:H layer.
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1. Introduction

An alignment layer is commonly used to line up liquid-crystal (LC) molecules along a certain direction in the liquid crystal display technology. A polyimide (PI) layer treated with mechanical rubbing, ion beam irradiation, or photo-alignment has been often used to enhance the LC alignment [1–7]. Amorphous carbon (a-C) is another potential material to replace PI as the alignment layer since it can achieve very good qualities such as uniformity, optical transparency, adhesion, and low deposition temperature [8]. The common a-C materials are hydrogenated amorphous carbon (a-C:H, <50% sp^3) and diamond-like carbon (DLC, >50% sp^3), defined by the concentration of sp^3 bonds [9].

The a-C material is too hard to use the traditional mechanical rubbing process for LC alignment. The ion beam irradiation at the oblique incidence has been reported to able to enhance the LC alignment on the a-C layer by Chaudhari et al. [10]. Recently, a plasma ion beam of elliptical shape provided by a plasma scanner has been developed for the LC alignment on the a-C layer [11,12].

Similar to ion beam irradiation, the oblique incidence of ions is crucial for a plasma ion beam treatment to favor the LC alignment. A bond-breaking process occurs on the surface of a-C due to the oblique incidence of ions, which is supported by experimental results of X-ray photoemission [12] and near edge X-ray absorption fine structure [13]. A subsequent formation of "directional" C–O bonds after the bond breaking process is considered to be able to enhance the LC alignment.

In this paper, we will present an alternative approach to enhance the LC alignment on the a-C:H layer immersed inside a plasma, rather than incident by an ion beam or a plasma ion beam. The a-C:H layer is treated inside the argon (Ar) plasma generated in a planar-type inductively coupled plasma (ICP) chamber. LC alignment occurs only for the a-C:H layer tilted at an angle during the ion bombardment inside the Ar plasma. No Kaufman ion beam [14,15] and focused plasma ion beam [11,12] facilities are required to generate the oblique incidence of ions.

2. Experimental details

The a-C:H layers of approximately 20 nm thick were deposited on the 60 Ω cm indium tin oxide (ITO) glasses (1.5×2 cm^2) in a

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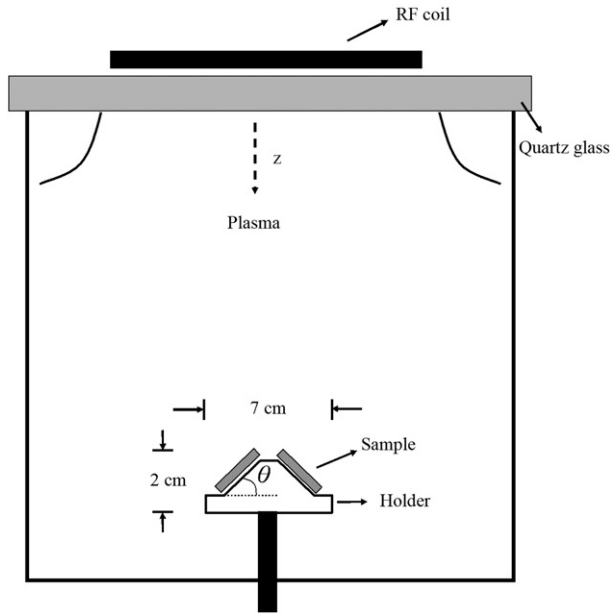E-mail address: jch@mx.nthu.edu.tw (J. Hwang).

Fig. 1. Schematic of the planar-type ICP chamber.

capacitive-coupled plasma-enhanced chemical vapor deposition chamber. The deposition parameters were designed to deposit uniform a-C:H layers of good Raman quality on the ITO glasses, which can be found in our previous work [12]. The as-deposited a-C:H layers were immersed in the Ar plasma in a planar-type ICP chamber for surface modification. Fig. 1 shows the schematic of the planar-type ICP chamber, in which the radio frequency (RF) coil was placed on a quartz glass outside the vacuum and the distance between the RF coil and the sample holder was approximately 28 cm. Three sample holders were designed such that the a-C:H layers were able to be tilted at two different angles (30° and 60°) during the Ar plasma ion immersion treatment. The as-deposited a-C:H layers were ion bomzbarded for 10 min inside the Ar plasma operated at a RF power of 200 W and at a working pressure of 5.87×10^{-1} Pa. The a-C:H layers were biased with a pulse voltage of -1000 V at a frequency of 100 Hz. The duration of each pulse voltage is 10 μs. The plasma density distribution at the operation condition was measured by a Langmuir probe made of a tungsten wire of 0.01 cm in diameter inserted inside a quartz tube. The chemical bond characteristics of the as-treated a-C:H films were measured by using X-ray photoemission spectroscopy (XPS, PHI 1600) equipped with a spherical capacitor analyzer. C $1s$ and O $1s$ core electrons were excited from the a-C:H films by Al K_α (1486.6 eV) at about 1.3×10^{-8} Pa. Two plasma-treated
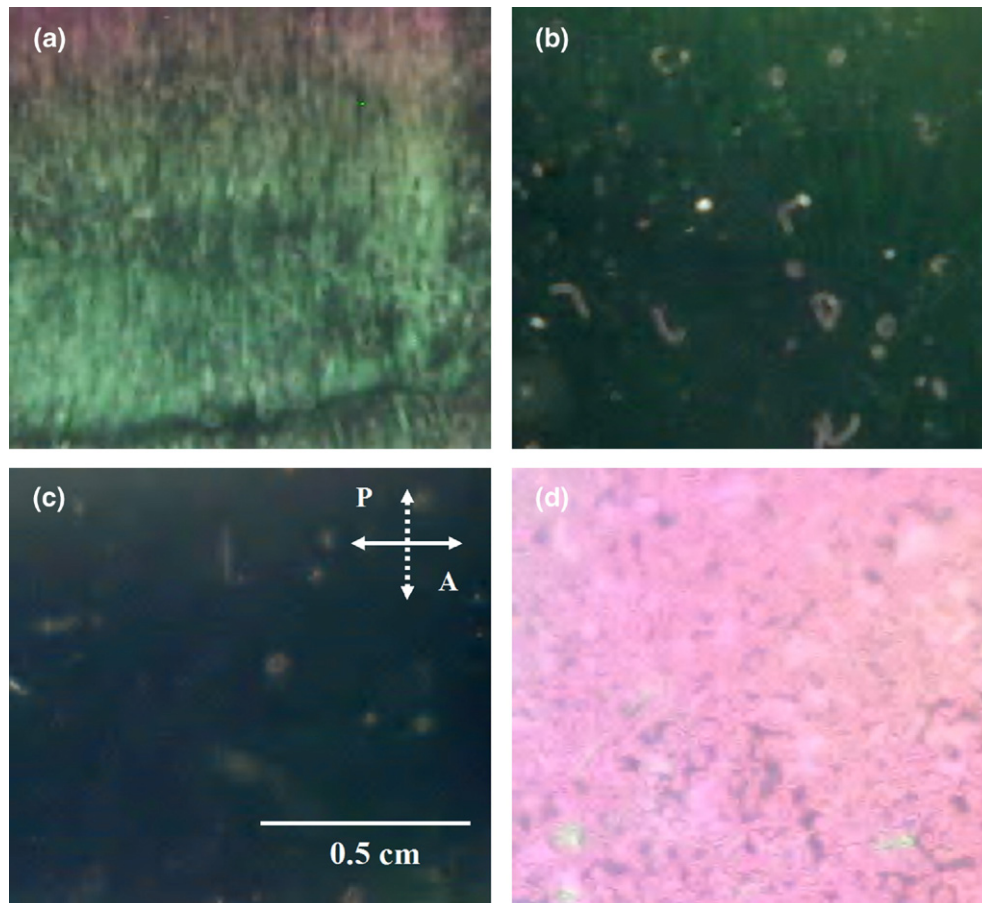

Fig. 2. Polarized optical photographs of liquid crystal TN cells observed with crossed polarizers. The a-C:H layers on the glass substrates in the TN cells are tilted upwards by the different angles during the Ar plasma ion immersion treatment: (a) 0°, (b) 30°, and (c) 60°. (d) The a-C:H layer is covered with a quartz glass during the Ar plasma ion immersion treatment at a tilted angle of 60°.

Table 1
LC alignment characteristics for the a-C:H layer treated with Ar plasma ion immersion in a planer-type ICP system

Samples	LC alignment	Tilt angle (deg)	Azimuthal anchoring strength (J/m^2)	Pretilt angle (deg)
a-C:H	No	0	–	–
a-C:H	Yes	30	1.98×10^{-6}	1.42
a-C:H	Yes	60	1.16×10^{-4}	1.47
Quartz/ a-C:H	Yes	60	–	–

a-C:H/ITO substrates were put together in an anti-parallel configuration to fill the nematic liquid crystal (Merck E-7). The anti-parallel LC cells were used to measure the pretilt angles at LC/a-C:H interfaces by crystal rotation method [16,17]. The uniformity of the LC alignment was characterized by a polarized optical charge-coupled display (Nikon coolpix 700). Twisted nematic (TN) cells, in which the plasma-treated a-C:H/ITO substrates were rotated to a 90° configuration, were also assembled to measure the azimuthal anchoring strengths at the LC/a-C:H interfaces [18,19].

3. Results and discussion

The anti-parallel LC cells exhibit different features of LC alignment for the a-C:H layers treated with Ar plasma ion immersion at different tilted angles, as shown in the polarized optical microscopy photographs presented in Fig. 2(a)–(c). No LC alignment (Fig. 2(a)) was observed for the a-C:H layer treated at a tilted angle of 0°. LC alignment (Fig. 2(b)) appears for the a-C:H layer treated at a tilted angle of 30°, indicating that the plasma ion immersion treatment at a tilted angle is in favor of LC alignment. However, many defect spots appear which are

attributed to the discontinuity of the LC alignment at those locations [20]. The contrast is also low, which probably resulted from the poor alignment of LC molecules on the a-C:H layer. The quality of LC alignment is greatly improved for the a-C:H layer treated at a tilted angle of 60°, as shown in Fig. 2(c). This implies that good LC alignment can be achieved by the plasma ion immersion treatment at an optimized tilted angle.

The pretilt angles and azimuthal anchoring strengths, characterizing the quality of LC alignment, exhibit different responses at the LC/a-C:H interfaces, which are tabulated in Table 1. The pretilt angle ($\sim 1.4°$) is approximately the same for different tilted angles. However, the azimuthal anchoring strength is 1.98×10^{-6} J/m^2 at a tilted angle of 30° and 1.14×10^{-4} J/m^2 at a tilted angle of 60°. The low azimuthal anchoring strength at 30° is consistent with the character of low contrast due to the poor alignment of LC molecules on the a-C:H layer. When the tilted angle increases from 30° to 60°, the azimuthal anchoring strength increases by two orders of magnitude. This suggests that the chemical bonding at the LC/a-C:H interface is more efficient, such that LC molecules are more difficult to rotate azimuthally for higher tilted-angle configuration. The high azimuthal anchoring strength suggests that most LC molecules are lined up with the easy axis, which is evident from the high contrast polarized optical microscopy photographs shown in Fig. 2(c).

The LC alignment is proven effective by tilting the a-C:H layer at an oblique angle during the Ar plasma ion immersion treatment. Two non-contact treatments, i.e. ultra-violet (UV) light and ion beams, have been reported to be able to enhance LC alignment [3–7]. In the Ar plasma, there exist UV light and plasma ions that possibly favor the LC alignment. The role of UV light in the LC alignment is excluded by the experiment described as follows. A piece of quartz glass was used to cover the a-C:H layer during the Ar plasma ion immersion at a tilted angle of 60° in order to isolate
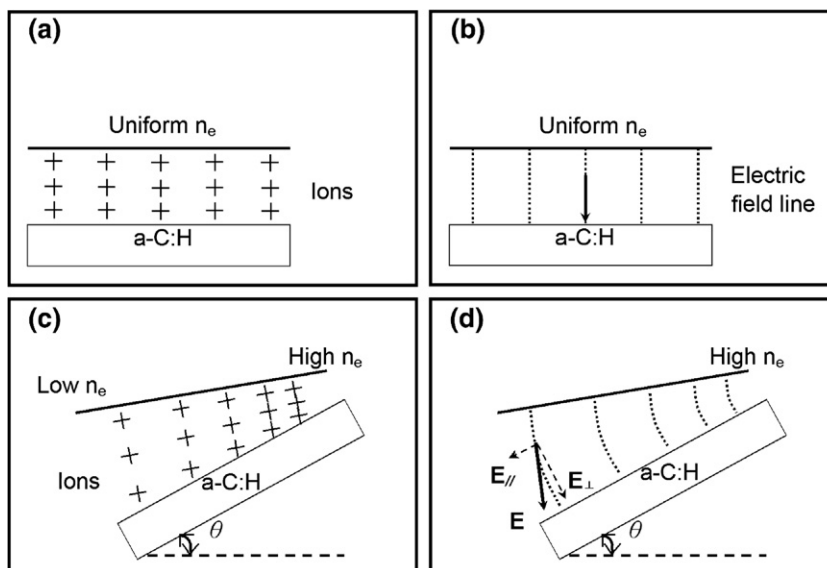

Fig. 3. Exaggerated sketches of the ion density distribution and the electric field lines inside the matrix sheath near the a-C:H layer biased with a negative pulse voltage immersed in the Ar plasma. The vectors are printed in boldface: (a) uniform ion density; at a tilted angle of 0°, (b) electric field line; at a tilted angle of 0°, (c) non-uniform ion density; at a tilted angle of θ, and (d) electric field line; at a tilted angle of θ. The plasma density (n_e) distribution in each case is also marked in the corresponding plot.
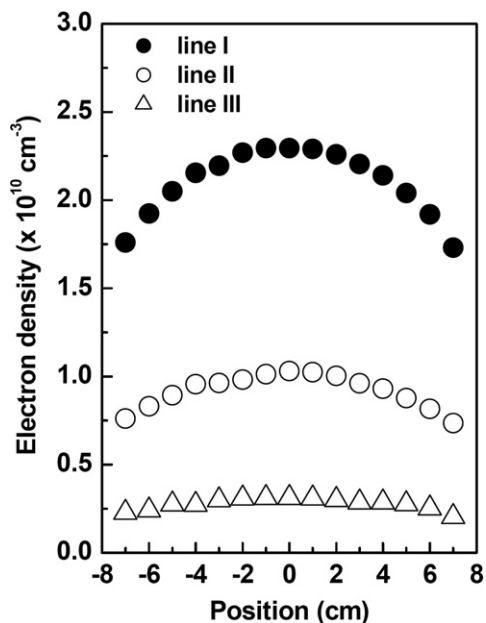
Fig. 4. Variation of plasma densities across the horizontal plane near the RF coil (line–I), near the middle of the chamber (line–II), and near the sample holder (line–III) inside a planar-type ICP chamber. The center position of the chamber is located at 0 cm.

the energetic ions and to allow the UV light to pass through. The transmittance of the quartz glass was determined to be 85% to 95% from 190 to 400 nm. Note that no LC alignment was observed as shown in Fig. 2(d). The LC alignment is thus proposed to be enhanced by the ion bombardment onto the a-C:H layer during the Ar plasma ion immersion.

As mentioned earlier, no LC alignment occurs for the a-C:H layer treated with Ar plasma ion immersion at a tilted angle of 0°, i.e. on the flat substrate holder. During the plasma ion immersion treatment, the a-C:H layer is under a pulse voltage of −1000 V for

$10 \, \mu s$ and under zero bias for the rest of time in each period. When the a-C:H layer is under the pulse voltage, electrons near the a-C:H layer are expelled suddenly such that ions left behind are uniformly distributed according to the plasma theory. The uniform ion density distribution in the sheath is exaggerated sketched in Fig. 3(a). The high-voltage sheath with a uniform ion density is known as the matrix sheath. The thickness of the matrix sheath is inversely proportional plasma density according to the equation below [21].

$$s = \left(\frac{2\varepsilon_0 V_0}{en_e} \right)^{1/2} \qquad (1)$$

where V_0 is the biased voltage, n_e is the plasma density, and ε_0 is the permittivity of vacuum. Note that the plasma density is uniform near the surface of the a-C:H layer at a tilted angle of 0°. The electric field is expected to be normal to the a-C:H layer, as shown in Fig. 3(b). All the ions inside the matrix sheath would be accelerated normally onto the a-C:H layer. This supports that normal incidence of ions onto the a-C:H layer results in no LC alignment.

When the tilted angle is changed to either 30° or 60°, the a-C:H layer is also immersed inside the plasma. A matrix sheath of uniform thickness is expected to form near the surface of the a-C:H layer if the plasma density is uniform. The electric field is also perpendicular to the surface of the a-C:H layer, which would result in a normal incidence of ions onto the a-C:H layer within the sheath. This is equivalent to the configuration at the tilted angle of 0° as shown in Fig. 3(a) and (b). In other words, no LC alignment should be observed. However, the appearance of LC alignment in Fig. 2(b) and (c) implies that ions are not normally incident onto the a-C:H layer. This suggests that there exists a mechanism for the oblique incidence of ion to occur within the sheath in our case.
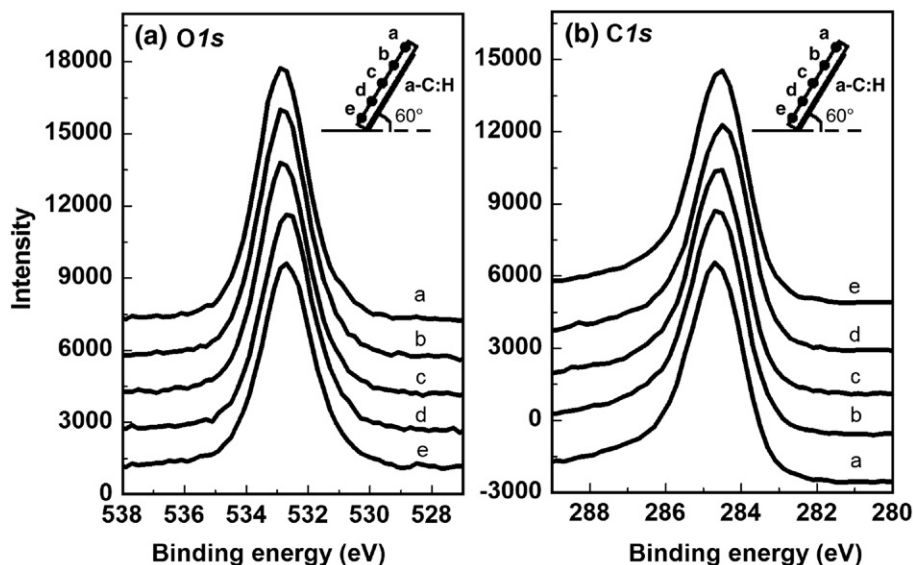

Fig. 5. XPS spectra of O 1s and C 1s emitted from different locations on the a-C:H layer treated with Ar plasma immersion at a titled angle of 60°. The location map for the XPS measurement is inserted in the upper-right corner. All the spectra were translated along the y-axis for clarity.

The oblique incidence of IONS is attributed to the matrix sheath of non-uniform thickness in our planar-type ICP plasma chamber, which is further confirmed by the plasma density measurement at the operation condition shown in Fig. 4. Along the chamber axis, the plasma density is about 2.3×10^{10} cm^{-3} near the RF coil, decreases to 1.1×10^{10} cm^{-3} near the middle of the chamber, and further decreases to about 3.1×10^9 cm^{-3} near the sample holder. The plasma density also slightly decreases away from the axis of the chamber, as shown in Fig. 4. For a tilting sample configuration, a matrix sheath of non-uniform thickness would be built up near the sample surface due to the non-uniform plasma density according to the Eq. (1). A narrow matrix sheath would form near high plasma density and a broad matrix sheath near low plasma density. The matrix sheath with the non-uniform ion density distribution is exaggeratedly sketched in Fig. 3(c). The electric field line is expected to be curved within the matrix sheath due to the constant potential inside the plasma and on the a-C:H surface. Within the matrix sheath, ions would be accelerated by the electric filed (E), which have both perpendicular ($E_\perp$) and parallel ($E_{//}$) components relative to the a-C:H surface as shown in Fig. 3(d). This would result in the oblique incidence of ions onto the a-C:H surface.

The non-uniform plasma density is also confirmed by the XPS spectra of the a-C:H layer treated with the Ar plasma immersion. Fig. 5(a) and (b) respectively shows the XPS spectra of O *1s* and C *1s* emitted from different locations on the a-C:H surface treated with Ar plasma immersion at a titled angle of 60°. The location-maps for the XPS measurement are respectively inserted in the upper-right corner in Fig. 5(a) and (b). The O *1s* peak is higher near the higher location and is lower near the lower location. This supports that the bond-breaking process is dense near the higher location such that the O *1s* peak is higher due to the reformation of C–O bonds after the breaking process. Plasma density is expected to be higher near the higher location and lower near the lower location. The bond-breaking process on the a-C:H surface along the tilting direction is also supported by the C *1s* spectra as shown in Fig. 5(b). The C *1s* peak is slightly lower near the higher location and slightly higher near the lower location. This implies that the reformation of C–O bonds is higher near the higher location. The existence of the non-uniform plasma density across the a-C:H layer along the tilting direction is thus further justified.

4. Conclusions

The LC alignment on the a-C:H layer has been achieved by the Ar plasma ion immersion in the planar-type ICP system. No ion gun is required for the LC alignment process as that in the ion beam irradiation treatments. The advantage of the plasma ion immersion process is the capability to scale up at a low cost. The mechanism to achieve the LC alignment is the non-uniform plasma density distribution in the planar-type ICP chamber which may induce a matrix sheath with non-uniform thickness near the a-C:H layer during a negative pulse bias. This would result in the oblique incidence of ions onto the a-C:H surface and favor the LC alignment.

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