Passivation effect on the liquid crystal alignment on a-C:H films: A two-step treatment by argon and hydrogen plasma beam scanning

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A two-step treatment by argon (Ar) and hydrogen plasma beam scanning was developed to modify the surface bonds of a hydrogenated amorphous carbon (a-C:H) film on indium tin oxide glass. The modified a-C:H film is an excellent layer for liquid crystal alignment, on which the pretilt angle of a nematic liquid crystal (ZLI-2293) can be adjusted by the two-step scanning treatment. The chemical bonding characteristics of the as-scanned a-C:H films were measured using micro-Raman and x-ray photoemission spectroscopies. The antiparallel cells were filled with the nematic liquid crystal on the as-scanned a-C:H film to measure the pretilt angle. Experimental results indicate that the carbon dangling bonds are generated through a bond-breaking process during the Ar plasma beam scanning step (first step). The hydrogen plasma beam scanning step (second step) can passivate some of the carbon dangling bonds that are generated in the first step. The pretilt angle decreases as the hydrogen plasma beam scanning time increases. The decrease of pretilt angle is due to the formation of C–H bonds that passivate the a-C:H film and limit the formation of C–O bonds in air. © 2007 American Institute of Physics. [DOI: 10.1063/1.2432044]

I. INTRODUCTION

Hydrogenated amorphous carbon (a-C:H) films have received much attention due to its potential as an excellent layer for liquid crystal (LC) alignment in liquid crystal display (LCD) technologies. An excellent layer for LC alignment generally requires good uniformity, high optical transparency, and strong adhesion. The polyimide (PI) film is the common alignment layer. However, it requires baking at ∼200 °C in order to evaporate the solvent after coating, which restricts to the selection of substrates with high melting point. The a-C:H film is a good potential material for replacing the PI film as the alignment layer because it exhibits a low deposition temperature (∼60 °C) in the capacitive-coupled plasma-enhanced chemical-vapor deposition (CPCVD) chamber. The a-C:H films also exhibit high mechanical hardness, chemical inertness, and strong adhesion to the indium tin oxide (ITO) glass, meeting the requirements of alignment layer. However, a-C:H films are usually darker than conventional PI films. The a-C:H films should be thin enough to exhibit high optical transmission in the visible range.

A traditional mechanical rubbing process on the a-C:H films does not exhibit LC alignment. Recently, two noncontact techniques, Kaufman ion beam and plasma beam scanning have been developed to improve the LC alignment for diamondlike carbon (DLC) or a-C:H films. The Kaufman ion beam is extracted and accelerated by the system of grids to bombard the alignment layer such that surface chemical bonds are modified. The ion energy of the Kaufman source is usually 50–150 eV. Stohr et al. proposed that carbon bonds and rings oriented perpendicular to the incident beam provide a larger cross section for the ion beam and are destroyed preferentially over those whose bonds or bonding planes are parallel to the beam direction. The amorphous carbon network exhibits a preferential orientation of its σ bonds parallel and π bonds perpendicular to the beam direction, respectively, as supported by the experimental result of near-edge x-ray absorption fine structure.

The method of LC alignment based on a treatment using an accelerated plasma beam was proposed by Yaroshchuk et al. Similar to Kaufman ion beam, a sheetlike plasma flux generated by an anode layer source was proven to be able to modify the surface of a-C:H films. Recently, a plasma beam scanner was developed to enhance the LC alignment for a-C:H films, in which an elliptical plasma beam was designed to scan across the substrate at a fixed angle of incidence. The plasma beam scanner is attractive since the anode layer source, in contrast to the Kaufman ion source, does not include any grids and heating elements that make it very reliable. In our previous work, the LC alignment on the a-C:H film treated with nitrogen plasma beam scanning has

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[Note: The text contains references to further reading and research, which are not displayed here.]
been demonstrated.\textsuperscript{7} A nitrogen plasma beam scanning treatment induces a bond-breaking process of aromatic rings to create available carbon dangling bonds for the formation of C–O bonds. The newly formed C–O bonds are considered to be “directional” because of the LC alignment in the beam scanning direction.

Based on the work on PI film by Sakuhara \textit{et al.}, the increase of pretilt angle is attributed to the increase of the dipole moment of surface bonds on the surface.\textsuperscript{9} This suggests that the pretilt angle can be varied by hydrogen passivation in order to reduce the amount of newly formed C–O bonds on the \(a\)-C:H film. The idea of the alignment layer passivation with reactive hydrogen was proposed by Katoh \textit{et al.} to reduce the aging phenomenon in the LC alignment.\textsuperscript{10} In 2005, the passivation of alignment layer with reactive hydrogen was realized by Yaroshchuk and co-workers.\textsuperscript{11,12} Their results support that hydrogen passivation can modify the surface bonds on the alignment layer.

In this article, we present a two-step plasma beam scanning process that can adjust the pretilt of the nematic liquid crystal (ZLI-2293) on the \(a\)-C:H film by varying the amount of C–O bonds. Argon (Ar) and hydrogen plasma beams are sequentially incident onto the \(a\)-C:H film at a fixed angle during scanning. The two-step treatment effectively reduces the amount of newly formed C–O bonds such that the corresponding pretilt angle is reduced.

\section*{II. EXPERIMENTAL PROCEDURE}

The \(a\)-C:H films were deposited on 30 cm\(\Omega\) ITO glasses in the CCP-CVD chamber. In a typical experiment, the CCP-CVD chamber was pumped down to a base pressure of \(\sim 1 \times 10^{-4}\) torr, and a mixture of 50\% CH\(_4\) and 50\% H\(_2\) (flow rate ratio) was fed into the chamber to ignite the CH\(_4\)/H\(_2\) plasma at a radio-frequency (rf) power of 100 W and a total pressure of 10 mtorr. The deposition time for each \(a\)-C:H film was set to 10 min in order to obtain the same thickness. The thicknesses of the \(a\)-C:H films were about 24 nm measured by a field-emission scanning electron microscope (JEOL-6500F). The carbon bonding characteristics of the films were measured using micro-Raman spectroscopy operated with a laser of 488 nm wavelength (Jobin-Yvon HR800). The micro-Raman laser beam was focused to a diameter of about 1 \(\mu\)m and the corresponding signal resolution was 0.4 cm\(^{-1}\). The laser power of the micro-Raman spectra was 25 mW and each integral time was set to 15 s.

A two-step treatment by Ar and hydrogen plasma beam scanning was performed on the as-deposited \(a\)-C:H films before the manufacture of a liquid crystal cell. The plasma beam chamber was first pumped down to a base pressure of \(\sim 1 \times 10^{-5}\) torr. In the first step, an Ar plasma beam, excited with a 500 V dc power supply at a total pressure of 0.2 mtorr, was incident on the as-deposited \(a\)-C:H film at a tilt angle of 20\(^{\circ}\) from the film surface. The Ar plasma beam was scanned forward and backward at a controllable speed of 6 mm/s during each scanning period. The working distance between the plasma beam and the substrate holder was about 20 cm. After the Ar plasma beam scanning, a hydrogen plasma beam was excited and scanned across the \(a\)-C:H film under the same experimental conditions in the second step. The surface morphologies of the as-treated \(a\)-C:H films were characterized using a DINS3a atomic force microscope (AFM). The chemical bond characteristics of the as-treated \(a\)-C:H films were measured by using micro-Raman and x-ray photoemission spectroscopy (XPS, PHI 1600). The antiparallel cells of \(2 \times 3\) cm\(^2\) \(a\)-C:H films were assembled to measure pretilt angles using the crystal rotation method\textsuperscript{13,14} (autronic-DMS 101). The antiparallel cells were constructed by putting together two pieces of the plasma-treated \(a\)-C:H substrate in an antiparallel configuration for LC filling.\textsuperscript{6} The antiparallel cells were filled with a nematic liquid crystal (ZLI-2293, Merck Taiwan Ltd) by capillary action, and the cell gap was kept at about 25 \(\mu\)m during filling. The uniformity of the LC alignment was characterized by a polarizing optical microscope (POM).

\section*{III. RESULTS AND DISCUSSION}

\subsection*{A. \(a\)-C:H films scanned with Ar plasma beam only}

The as-deposited \(a\)-C:H films exhibit no LC alignment as shown in the POM photograph in Fig. 1(a). LC alignment occurs when \(a\)-C:H films are treated with Ar plasma beam scanning. Figure 1(b) shows a typical POM photograph of a cell with LC alignment, in which the \(a\)-C:H films are treated with Ar plasma beam scanning for 20 s. All of the POM photographs obtained with scanning time over 20 s were almost identical.
Figure 2 shows the variation of the pretilt angle with scanning time for the a-C:H film during Ar plasma beam scanning. The pretilt angle is in the range of 2.5±0.5°, and increases slightly with scanning time. Note that no LC alignment occurs for the as-deposited a-C:H film, observed by POM photographs. LC alignment is induced by the Ar plasma beam scanning process. In order to investigate the possible mechanism for the LC alignment, AFM is applied to find grooves potentially on the as-scanned a-C:H film. No apparent surface grooves were observed on a-C:H films scanned with the Ar plasma beam. The grooving mechanism seems to be not a major factor in the LC alignment on the a-C:H films.

Similar to our previous work using nitrogen plasma beam scanning,7 the LC alignment is attributed to the “newly formed C–O bonds” on the surface of the as-scanned a-C:H film. No apparent surface grooves were observed on a-C:H films scanned with the Ar plasma beam. The grooving mechanism seems to be not a major factor in the LC alignment on the a-C:H films.7 Similar to our previous work using nitrogen plasma beam scanning,7 the LC alignment is attributed to the “newly formed C–O bonds” on the surface of the as-scanned a-C:H film during exposure to air. The existence of the newly formed C–O bonds is supported by the XPS spectra in Fig. 4.

Figure 3 shows the micro-Raman spectra of a-C:H films scanned with an Ar plasma beam. All of the Raman spectra of the a-C:H thin films exhibit two major peaks—the D band (centered at ~1350 cm⁻¹) and the G band (centered at ~1580 cm⁻¹). The D band arises from disordered graphite due to the A₁g vibration mode, and the G band arises from graphite due to the E₂g vibration mode.15–18 All C=–C chains or aromatic rings may contribute G mode intensity due to the stretching vibration of sp² sites, and only those in the aromatic rings could increase the intensity of the D mode due to the breathing mode of those sp² sites.16–18 Another Raman peak at 1490 cm⁻¹ usually accompanies D and G peaks, and is associated with the semicircle ring stretch vibration of the C–H in a-C:H.19 All of the Raman spectra in Fig. 3 are curve fitted by the three peaks to extract the variation of chemical bonds due to the plasma beam scanning treatment. The I(D)/I(G) ratios of the a-C:H films are determined to be 0.36, 0.35, 0.35, 0.34, and 0.33 for Ar plasma beam scanning times of 0, 20, 40, 60, and 80 s. The slight reduction of I(D)/I(G) indicates that a breaking process of aromatic rings occurs on the surface during Ar plasma beam scanning. The bond-breaking process creates carbon dangling bonds, which are available for further formation of C–O bonds, as confirmed by the XPS spectra in Fig. 4.

Figures 4(a) and 4(b), respectively, show the O₁s and C₁s core level spectra excited by Al Kα (1486.6 eV) for a-C:H films scanned with the Ar plasma beam. Similar to our previous work,7 a-C:H films exhibit slight charging such that all the core level peaks move to higher binding energy by ~2.1 eV. The energies of the O₁s and C₁s core levels are thus calibrated according to this amount. The O₁s intensity in Fig. 4(a) slightly increases with scanning time, implying that C–O bonds are newly formed on the a-C:H film. The C₁s intensity in Fig. 4(b) stays about the same with scanning time. The C₁s core level spectra can be deconvoluted into C–C, C–H, and C–O components. The relative amounts of the three components at different scanning times are listed in Table I. The amounts of both C–H and C–C bonds at different scanning times are approximately equal. The C–O component increases with scanning time, confirming that C–O bonds are newly formed on the as-scanned a-C:H film.

Note that no LC alignment occurs for the a-C:H films without Ar plasma beam scanning. The a-C:H films scanned...
with Ar plasma beam exhibit LC alignment. Sakuhara et al.\textsuperscript{9} proposed that pretilt angle can be affected by the dipole moment of chemical bonds on the surface. The amount of C–O bonds in Table I increases slightly with scanning time, like the time response function of the pretilt angle in Fig. 2. The newly formed C–O bonds are considered to be closely correlated to the pretilt angle, suggesting that the pretilt angle can be adjusted by varying the amount of newly formed C–O bonds on the $a$-C:H film.

**B. $a$-C:H films scanned sequentially with Ar and hydrogen plasma beams**

The pretilt angle of an $a$-C:H film can be fine-tuned by hydrogen plasma beam scanning (second step) followed by Ar plasma beam scanning (first step). All the $a$-C:H films treated with the two-step plasma beam scanning exhibit uniform LC alignment, similar to that in the POM image in Fig. 1. Figure 5 shows the variation of pretilt angle with scanning time after the hydrogen plasma beam scanning treatment for the $a$-C:H film pretreated with Ar plasma scanning for 40 s. The pretilt angle decreases from $\sim 2.5^\circ$ to $\sim 1.5^\circ$ as the scanning time increases from 40 to 120 s. The intensity of O$_{1s}$ at $\sim 532.5$ eV decreases as the scanning time increases. Notably, the O$_{1s}$ signal is taken when the as-scanned $a$-C:H film is exposed to air after the two-step plasma beam scanning treatment. Newly formed C–O bonds are expected to be observed when the as-scanned $a$-C:H film is reexposed to air. The reduction of O$_{1s}$ intensity with increasing scanning time in Fig. 6(a) implies that the formation of newly formed C–O bonds is limited by the hydrogen plasma beam scanning treatment. Very probably, C–H bonds are formed near the surface of the $a$-C:H film during hydrogen plasma beam scanning (second step), preventing the formation of the C–O bonds in air. In other words, the $a$-C:H film surface is passivated during hydrogen plasma beam scanning. The hydrogen passivation is further confirmed by the reduction of C–O bonds and the increase of C–H bonds in the deconvoluted C$_{1s}$ spectra as shown in Fig. 6(b). The relative amounts of C–C, C–H, and C–O components deconvoluted from the C$_{1s}$ spectra in Fig. 6(b) are tabulated in Table II. The intensity of the C–O bonds decreases as scanning time increases, and is accompanied by an increase in the amount of C–H bonds. This result is an evidence of hydrogen passivation on the $a$-C:H film, which limits the formation of C–O bonds.

As mentioned earlier, the amount of newly formed C–O bonds is closely correlated to pretilt angle. The pretilt angle in Fig. 5 falls as the hydrogen plasma beam scanning time increases, as does the amount of the C–O bonds. The reduction of newly formed C–O bonds is considered to be the

![FIG. 5. LC pretilt angles for the $a$-C:H films at different scanning times in hydrogen plasma beam scanning processes (second step). The scanning time for the Ar plasma beam scanning (first step) is fixed at 40 s.](image)

![FIG. 6. Core level spectra of the $a$-C:H films treated with Ar plasma beam scanning for 40 s and followed by hydrogen scanning time for 20, 60, 80, and 100 s, (a) O$_{1s}$ and (b) C$_{1s}$. The C$_{1s}$ spectra are deconvoluted into the C–C, C–H, and C–O components.](image)

**TABLE I. Relative amounts of the C–C, C–H, and C–O bonds deconvoluted from the C$_{1s}$ core level spectra [Fig. 4(b)] of the $a$-C:H films treated with Ar plasma beam scanning.**

<table>
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<tr>
<th>Components</th>
<th>0 s</th>
<th>20 s</th>
<th>40 s</th>
<th>60 s</th>
<th>80 s</th>
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<tbody>
<tr>
<td>O$_{1s}$</td>
<td>100%</td>
<td>124%</td>
<td>129%</td>
<td>126%</td>
<td>131%</td>
</tr>
<tr>
<td>C$_{1s}$</td>
<td>100%</td>
<td>103%</td>
<td>94%</td>
<td>95%</td>
<td>106%</td>
</tr>
<tr>
<td>C–C bonds</td>
<td>100%</td>
<td>104%</td>
<td>90%</td>
<td>92%</td>
<td>101%</td>
</tr>
<tr>
<td>C–H bonds</td>
<td>100%</td>
<td>92%</td>
<td>90%</td>
<td>90%</td>
<td>96%</td>
</tr>
<tr>
<td>C–O bonds</td>
<td>100%</td>
<td>114%</td>
<td>124%</td>
<td>132%</td>
<td>138%</td>
</tr>
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</table>
cause of the reduction of the pretilt angle. This result suggests that the pretilt angle is proportional to the dipole moment of newly formed C–O bonds. Overall, hydrogen passivation provides a way to adjust the amount of newly formed C–O bonds that varies the pretilt angle as a consequence.

IV. CONCLUSION

A two-step treatment by Ar and hydrogen plasma beam scanning has been developed to vary the pretilt angle of a nematic liquid crystal (ZLI-2293) on the a-C:H film. Ar ions are incident on the a-C:H film, such that carbon dangling bonds are generated through a bond-breaking process during the Ar plasma beam scanning step (first step). The carbon dangling bonds are usually oxidized to form C–O bonds when the a-C:H film is exposed to air. The hydrogen plasma beam scanning step (second step) passivates some of the carbon dangling bonds generated in the first step. This can adjust the amount of C–O bonds after exposure to air, which is closely correlated to the pretilt angle of the nematic liquid crystal (ZLI-2293) on the a-C:H film. The work regarding the modification of C–O bonds on the a-C:H films suggests that surface bond engineering is important in the LC alignment.

ACKNOWLEDGMENTS

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TABLE II. Relative amounts of the C–C, C–H, and C–O bonds deconvoluted from the C1s core level spectra [Fig. 6(b)] of the a-C:H films treated with Ar and hydrogen plasma beam scanning. The scanning time for the Ar plasma beam scanning (first step) is fixed at 40 s.

<table>
<thead>
<tr>
<th>Components</th>
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<td></td>
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<tr>
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<td>100%</td>
</tr>
<tr>
<td>C1s</td>
<td>100%</td>
</tr>
<tr>
<td>C–C bonds</td>
<td>100%</td>
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<tr>
<td>C–H bonds</td>
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<tr>
<td>C–O bonds</td>
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