Liquid Crystal Alignment on Plasma Beam Scanned Alkyldimethoxyxilane Self-Assembled Monolayers


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A capacitive coupled plasma chemical vapor deposition chamber. The a-C:H films were first deposited on 30 cm diameter indium tin oxide (ITO) glasses in an absolute alcohol solvent. The SAM deposition is a simple process compared to polymer deposition processes. In contrast, polymer films require baking at 150–200°C after spin coating to evaporate solvent and to induce polymerization. Second, the thickness of SAM is very uniform because at most one SAM layer can be deposited on the glass by its functional group bonding with silica. In 2001, Lee et al. proposed that SAM could achieve nematic LC alignment by UV light irradiation. Mechanical rubbing and plasma treatment were also found effective in modifying the surface of SAM in favor of LC alignment. In 2002, Balwa et al. improved smectic LC alignment on octadecyl-triethoxysiloxane (OTMS) SAM deposited on the glass by mechanical rubbing. Mechanical rubbing induced a tilt direction of the octadecyl chains in the SAM to achieve homeotropic alignment. Later, in 2003, Fonseca et al. reported that homogeneous or homeotropic alignment occurred on OTMS SAM modified by a plasma of O2/N2. Varying the concentration of oxygen grafted onto the SAM surface, a fast anchoring transition between homeotropic and homogeneous (planar) alignment was observed.

The octadecyl-trimethoxyxilane self-assembled monolayers (SAMs) exhibit better uniformity and smoothness on hydrogenated amorphous carbon (a-C:H) films than on indium tin oxide glasses. The liquid crystal alignment on the SAM/a-C:H can be greatly improved by Ar plasma beam scanning. The prettilt angle increases abruptly with Ar plasma beam scanning time within 5 s and reaches a maximum value of about 5° at a longer scanning time. The surface roughness of SAM slightly increases from 0.10 to 0.13 nm after Ar plasma beam scanning. This implies that bond breaking occurs on the SAM surface during the plasma beam scanning. Fourier transform infrared spectrometer and X-ray photoemission spectroscopy data indicate that plasma beam scanning can sputter off the CH2 bonds in the alkyl chain of SAM. The amount of oxygen on the SAM surface increases after plasma beam scanning and the increase of oxygen is attributed to the formation of C–O bonds during air exposure after plasma beam scanning.

The zenithal anchoring (prettilt) angle is strongly correlated with the oxygenated functions on the SAM layer based on their X-ray photoelectron spectroscopy (XPS) data.

Recently, Yaroshchuk et al. reported that a sheetlike plasma source was able to modify the surface of a PI film for LC alignment. The sheetlike plasma source was further modified into a plasma beam scanner, where a plasma beam of elliptical shape was designed to scan across the alignment layer at a fixed angle of incidence. The plasma beam scanning technique was effective in improving the LC alignment on hydrogenated amorphous carbon (a-C:H) and PI alignment layers. It is of interest to investigate whether LC alignment occurs on the SAM treated with plasma beam scanning or not.

In this study, OTMS SAM was deposited on the a-C:H film on an indium tin oxide (ITO) glass in an absolute alcohol solvent. The deposition of a-C:H on the ITO glass is required to prevent the ITO layer from being etched off in a mixed solution of H2O2/H2SO4 prior to the SAM deposition. The surface of the SAM was treated with an elliptical beam of plasma for different periods of scanning time. The LC cells made of the plasma beam scanned SAM exhibit homogeneous LC alignment. The interaction between the plasma beam and SAM has been investigated by atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectrometry, and XPS.

**Experimental**

The a-C:H films were first deposited on 30 cm diameter ITO glasses in a capacitive coupled plasma chemical vapor deposition chamber. The chamber was pumped down to a base pressure of ~1 × 10⁻⁴ Torr, and a mixture of 50% CH2 and 50% H2 (flow rate ratio) was fed into the chamber to ignite the CH2/H2 plasma at a radio-frequency 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 to obtain the same thickness of 24 nm measured by a field-emission scanning electron microscope (JEOL-JSM6500F).

The a-C:H films were immersed in a mixed solution of H2O2 and H2SO4 (1:1 v/v) to generate hydroxyl groups on the surfaces. After 15 min immersion, the hydroxyl surfaces of a-C:H films were washed by deionized water and dried by nitrogen stream. The a-C:H films were immersed in a 10 mM OTMS solution for 10 min and then placed in air for 24 h to obtain uniform SAMs on a-C:H films. The redundant OTMS molecules on the surface of the SAMs were further washed by absolute alcohols. The alkylsiloxane SAMs were then attached on the a-C:H films.

An Ar plasma beam scanning treatment was then performed on the as-deposited SAM/a-C:H prior to the manufacture of LC cells. The plasma beam chamber was first pumped down to a base pres-
sure of $\sim 1 \times 10^{-5}$ Torr. The Ar plasma beam, excited with a 500 V dc power supply at a total pressure of 0.2 mTorr, was incident onto the SAM/a-C:H at a tilted angle of 20° from the film surface. The Ar plasma beam was scanned across the SAM/a-C:H at a controllable speed of 6 mm/s during each scanning period. The working distance between the plasma beam and the SAM/a-C:H was kept at about 20 cm.

The antiparallel cells of $2 \times 3$ cm$^2$ SAM/a-C:H were assembled to measure pretilt angles using the crystal rotation method (autronic-DMS 101). A nematic LC (ZLI-2293, Merck Taiwan Ltd.) was filled in the cell by capillary action, and the cell gap was kept at about 25 µm during filling. The quality of LC alignment on the SAM/a-C:H was observed by a polarizing optical microscope (POM). The surface morphologies of SAM were characterized using a DINS-IIIa AFM. The chemical bond characteristics of the SAM were measured by using transmission mode FTIR (Bomem, DA8.3, 4 cm$^{-1}$ resolution) and XPS (PHI 1600).

Results and Discussion

Figures 1a and b are the POM images showing the quality of the alignment of LC molecules in the LC cells made of SAM/a-C:H treated with Ar plasma beam scanning for 0 and 40 s, respectively. The SAM/a-C:H without plasma beam scanning exhibits a poor LC alignment. The LC molecules cannot block the polarized light completely with a crossed polarizer and an analyzer. When the SAM/a-C:H is treated with plasma beam scanning for 40 s, the LC alignment is greatly improved. LC molecules completely block the polarized light. The plasma beam scanning treatment is efficient in modifying the surface of SAM/a-C:H in favor of LC alignment. By varying the plasma beam scanning time, all LC cells made of the plasma scanned SAM/a-C:H exhibit about the same LC alignment quality. Figure 2 shows the pretilt angle of LC molecules in the LC cell made of SAM/a-C:H treated with different Ar plasma beam scanning time. The pretilt angle increases abruptly with Ar plasma beam scanning time within 5 s and reaches a maximum value of about 5° at a scanning time longer than 10 s.

The surface roughness of SAMs is an important property to evaluate the uniformity of SAMs on a substrate. Figure 3a is the AFM image showing the morphology of the SAM deposited on the a-C:H film. The surface roughness of the SAM was determined to be 0.10 nm. The surface of the a-C:H is hydroxylated in a mixed solution of H$_2$O$_2$/H$_2$SO$_4$ prior to the SAM deposition, resulting in a small surface roughness of SAM. In contrast, the surface roughness
of the SAM increases from 0.1 to 0.74 nm when SAM is deposited on an ITO glass, as shown in Fig. 3b. The increase of surface roughness is attributed to the etching of ITO immersed in a solvent of H₂O₂/H₂SO₄ prior to the SAM deposition. This is supported by an XPS analysis showing that no indium or tin signals of ITO glasses were detected after the SAM deposition. Figure 3c is the AFM image showing the morphology of the SAM treated with Ar plasma beam scanning for 40 s. The surface roughness of the SAM slightly increases from 0.10 to 0.13 nm after Ar plasma beam scanning. This implies that bond breaking occurs on the SAM surface during the plasma beam scanning.

The bond-breaking information during the plasma beam scanning can be characterized by FTIR and XPS analyses. Figure 4 shows the FTIR spectra of the SAM treated with Ar plasma beam scanning for 0 and 40 s. Because ITO glasses interfere with the infrared signals in the range of 500–4000 cm⁻¹, the FTIR analysis, the SAM/a-C:H film was thus deposited on a polished silicon wafer to remove the interference signals. Three major signals of SAM, i.e., the Si–C bond at 728 cm⁻¹, the Si–O bond at 1020 cm⁻¹, and the CH₂ bond at 2850 and 2920 cm⁻¹, clearly appear in the FTIR spectrum of the SAM/a-C:H without plasma beam scanning. The intensity of the CH₂ bonds decreases after Ar plasma beam scanning, indicating that Ar plasma beam can sputter CH₂ bonds off the alkyl chain of a self-aligned alkylsiloxane molecule. The slight reduction of Si–O bond intensity at 1020 cm⁻¹ and Si–C bonds at 728 cm⁻¹ occurs. The spatial positions of Si–O and Si–C bonds are close to the surface of a-C:H film. This indicates that Ar plasma beam can break chemical bonds located at a deeper position of an SAM. The sputter depth of the plasma beam scanning on SAM will be discussed in detail using XPS spectra.

Figures 5a-c, respectively, shows the core level spectra of Si₂p, C₁s, and O₁s excited by Mg Kα (1253.6 eV) for the SAM treated with different plasma beam scanning time. The intensities of Si₂p and O₁s are very small compared to that of C₁s. Both Si₂p and O₁s signals are then amplified by a normalization process for clarity. All core level spectra of Si₂p, C₁s, and O₁s shift to a lower binding energy as the plasma beam scanning time increases. The energy shift reaches a maximum value of about 2.2 eV at 80 s for all the core level spectra. An energy shift in XPS can be resulted from either chemical shift or charging. Not all the core level spectra would shift toward the same amount of energy if a chemical shift occurred. The energy shift is thus attributed to the slight charging on the SAM/a-C:H/ITO glass. Note that the thickness of the SAM is about 2.5 nm. And, the escape depth (λ) of a photoexcited electron from SAMs can be estimated by the equation $\lambda = \frac{0.9 + 2.2 \times 10^{-3} E_k}{E_k}$, where $E_k$ is the kinetic energy of the photoexcited electron. The escape depths of Si₂p, C₁s, and O₁s excited by Mg Kα are estimated to be about 3.44, 3.03, and 2.46 nm, respectively. The photoelectron signals from SAMs can be completely detected by a spherical capacitor analyzer of XPS because its thickness is less than the escape depth. The charging-induced energy shift is expected to decrease when the thickness of the SAM decreases after plasma beam scanning. This is exactly the case observed in Fig. 5a-c. The observance of the Si₂p signal in Fig. 5a confirms the FTIR data of SAMs in Fig. 4, indicating that the alkylsiloxane SAM is attached on the a-C:H film. Moreover, the Si₂p signal reduces in intensity with increasing plasma beam scanning time and disappears at 80 s. This confirms that SAMs can be completely sputtered off the a-C:H film by Ar plasma beam scanning. The sputtering of SAMs results in interesting features in the C₁s signal in Fig. 5b. The intensity of C₁s reduces...
The decrease of O 1s from 10 to 80 s occurs almost simultaneously with the reduction of the Si 1s signal in the previous study on a-C:H films, the O1s signal at 80 s may come from the SAM molecule are completely sputtered off the a-C:H surface exhibit no preferred oriented direction, resulting in a poor LC alignment. The role of plasma beam scanning is to sputter CH 2 bonds in the alkyl chain at a scanning time longer than 5 s. The amount of oxygen on the SAM increases after plasma beam scanning and the oxygenated SAM surfaces play an important role in LC alignment. The increase of oxygen is attributed to the formation of C–O bonds during air exposure after plasma beam scanning.

Note that LC alignment occurs at 80 s although the SAM completely disappears at 80 s. The LC alignment at 80 s is certainly due to the plasma beam scanned a-C:H films, rather than SAM.

The model of atomic arrangements of SAMs without and with a typical Ar plasma beam scanning time (20 s) is proposed in Fig. 6a and b, respectively. Prior to the SAM deposition, the surface of the a-C:H film adsorbs some oxygen atoms during the hydroxyl process. The Si atoms of an SAM are bonded with the C–O bonds of the a-C:H film as shown in Fig. 6a. The LC molecules on the SAM surface exhibit no preferred oriented direction, resulting in a poor LC alignment. The role of plasma beam scanning is to sputter CH 2 bonds off the SAM and to generate a new SAM surface with anisotropic chemical bonds. The plasma beam scanned SAM surface thus favors LC alignment as plotted in Fig. 6b. The existence of anisotropic orientation of chemical bonds is supported by an indirect argument that the very good quality of LC alignment occurs only after plasma beam scanning along a certain (anisotropic) direction.

Conclusion

An Ar plasma beam scanning treatment is effective in improving the LC alignment on the alkylsiloxane SAM. The prettilt angle increases abruptly with Ar plasma beam scanning time within 5 s and reaches a maximum value of about 5° at a longer scanning time. Both FTIR and XPS data support that Ar plasma beam scanning can sputter off the CH 2 bonds in the alkyl chain at a scanning time longer than 5 s. The amount of oxygen on the SAM increases after plasma beam scanning and the oxygenated SAM surfaces play an important role in LC alignment. The increase of oxygen is attributed to the formation of C–O bonds during air exposure after plasma beam scanning.

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References