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Liquid Crystals

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A chemically modulated polystyrene surface for homogeneously aligned liquid crystals using various ion beam exposure angles

Jeong-Hwan Kim^a, Hong-Gyu Park^a, Young-Gu Gang^a, Ji-Hun Lim^a, Jeong-Yeon Hwang^a, Chul-Ho Ok^a, Dae-Shik Seo^a*, Jeong-Min Han^b, Sung-Ho Kim^c and Tae-Kyu Park^c

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In this study, transparent polystyrene (PS) was replaced with conventional polyimide material. As a non-contact process, an ion beam (IB) bombardment process was applied to align the homogeneous liquid crystal (LC) material on the PS surfaces. Confirming the atomic force microscopy and X-ray photoelectron spectroscopy analysis, the chemical compositional changes of the IB-irradiated PS surfaces were determined as a function of the IB exposure angle although there was no effect of modulation of the physical geographic characteristics on IB-irradiated PS surfaces. Using this analysis, the optimal IB bombardment condition was determined at the IB exposure angle of 45°. Finally, the electro-optical properties of an LC cell suggest the use of PS in conventional LC alignment materials.

Keywords: ion beam; plasma; polystyrene; liquid crystal; XPS

1. Introduction

Polyimide (PI) materials have widely been used as a liquid crystal (LC) alignment layer in liquid crystal displays (LCD) [1–6]. In this study, polystyrene (PS) was used as a substitute material for a LC alignment layer. PS is a commonly used plastic, but recently the use of PS films has expanded so that it now has several applications, such as in LCD phase compensation film, non-volatile memory devices, biosensors and so forth, due to its own characteristics [7-9]. In addition, PS has been adopted because of its potential as a candidate for a LC alignment layer in previous research [10]. Moreover, an ion beam (IB) bombardment process was used instead of the conventional rubbing process. The rubbing process has serious issues, such as debris, uneven roller traverse and electrostatic discharge, which produce the effects of local streaks, defects and the consequent degradation of the display. Although there are many non-contact methods available, including oblique deposition [11–13], nanoimprint lithography [14], UV exposure [15-17] and nanostructured alignment surfaces [18], we used a Duo-PIGatron IB device with a uniform, dense Ar⁺ plasma environment, which provides controllability, a continuous process and a high-resolution display [19].

As an LC alignment material, the refractive index of PS is nearly the same as that of glass substrate, implying that the transparent PS material is a candidate for an organic alignment material. To align the homogeneous LC molecules on the PS layers, IB irradiation as a

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function of IB exposure angle was used. Observing the conditions of the homogeneously aligned LC molecules helped to determine the optimal IB exposure angle. Additionally, the physical and chemical changes before and after the IB irradiation process on the PS surfaces were examined using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) analysis. Finally, the electro-optical (EO) properties were evaluated to confirm the proper LC driving characteristics.

2. Experiment

Indium tin oxide (ITO)-coated glass substrates were cleaned supersonically in trichloroethylene-acetonemethanol-deionised water solution sequentially for 15 min. The substrates were then dried with N2 gas. PS materials were coated uniformly onto the cleaned ITOcoated glass substrates using a spin-coating process. Figure 1 shows the molecular structure of PS. The PScoated substrates were soft-baked at 80°C for 10 min and imidised at 230°C for 1 h. The IB bombardment was conducted at angles of 15, 30, 45, 60, and 75° with an exposure energy and time of 2 keV and 1 min, respectively. To measure the pretilt angles of the homogeneous LC molecules on the IB-irradiated PS surfaces, a crystal rotation method (TBA 107 Tilt-bias Angle Evaluation Device; Autotronic) was used, observing the oscillation of the transmittance of LC cells (60 μ m cell gap) with a latitudinal rotation from -70° to 70° through the variation of the birefringence produced by



Figure 1. The molecular structure of PS.

LC cell rotation [20]. All IB-irradiated PS surfaces were examined using XPS (ESCA LAB 220-XL, VG Scientific, USA) analysis. The measured bindings were referred to the C 1s signal at 284.6 eV, and the composition of each sample was determined to compare the normalised area intensities of the C 1s peaks. Moreover, PS surfaces were investigated using AFM (AutoProbe CP research System, ThermoMicroscopes) to confirm whether IB bombardment affects morphology. Contact angles were measured using a Rame-Hart telescopic goniometer and a Gilmont syringe with a 25-gauge flat-tipped needle using a contact analyser (Phoenix 450, Surface Elec-tro Optics, Seoul, Korea). Distilled water was used as the probe fluid. Finally, twisted-nematic (TN) LCDs (5 µm cell gap) on the IB-irradiated PS surface were fabricated to measure the electro-optical (EO) properties of the transmittance and response time (RT) via the applied AC voltage signal.

3. Results and discussion

Figure 2 shows the observed tilt angles of homogeneous LCs. The curve in Figure 2 is similar to that observed in our previous studies. It could be confirmed, however, that the error values of the tilt angles



Figure 2. The measured tilt angles of homogeneous LC molecules on IB-irradiated PS surfaces on ITO-coated glass substrates. The tilt angles each have an associated error value.

depended more strongly on the IB exposure angle in the case of PS films than was the case with other materials. This means that PS material is very sensitive to the condition of IB bombardment during the alignment of LC molecules.

Figure 3 shows the photomicroscopes of the LCDs on IB-irradiated PS surfaces as a function of the IB exposure angle. In Figure 2, the error bar indicates whether the LC molecules are clearly aligned on the PS surfaces. Figure 3 reveals that the optimal IB exposure angle was 45°, because it yielded the clearest image and produced the smallest error value, as shown in Figure 2. A clear and stable image suggests that the PS material is appropriate for aligning LC molecules with the transparency property.

Generally, IB exposure in an Ar^+ plasma environment is used to etch a deposited layer. This suggests the assumption that the physical modulation contributed to the alignment of the LC molecules. To confirm the assumption, AFM was applied to the IB-bombarded PS surfaces. As Figure 4 shows, the measured values of the RMS (root-mean-square) traced out the curve in Figure 2 in reverse, revealing that the IB



Figure 3. Photomicrographs of LCDs on the IBirradiated PS surfaces at IB exposure angles of (a) 15° , (b) 30° , (c) 45° , (d) 60° and (e) 75° with an IB energy of 2 keV and an exposure time of 1 min (colour version online).



Figure 4. The measured RMS values on IB-irradiated PS surfaces as a function of IB exposure angle. IB energy and time were fixed to 2 keV and 1 min, respectively.

bombardment modulates the physical properties of the PS surfaces. In particular, the IB bombardment might produce anisotropic grooves along the direction of the IB process, which might also align the homogeneous LC molecules.

Figure 5(a) shows the measurement of the contact angle for the observed microphotographs of the IBbombarded PS surfaces. Processing the IB bombardment on PS surfaces, we observed that the contact angles were smaller than those on a non-IB-processed PS surface. Moreover, the curve in Figure 5(a) traced out the curve in Figure 2 in reverse, indicating that the surface energies on IB-bombarded PS surfaces could explain the alignment of the homogeneous LC molecules, as the contact angle is closely related to the surface energy [21].

The XPS spectra were investigated to confirm that IB bombardment caused the chemical reaction on the PS surfaces, because a chemical reaction such as bonding breaking could modulate the surface energy. The chemical binding characteristics of atoms on the PS

surfaces were analysed using the XPS spectra of C 1s and O 1s core levels [22-24]. Figure 6 shows the measured C 1s spectra, in which the dominant peak component of the aromatic carbon area was located at 284.5 ± 0.1 eV. The component peak at 285 ± 0.1 eV is related to the C_H atoms, and the low binding energy at 282.3 \pm 0.1 eV is due to the surface contamination of C 1s. The component peak located at 286.4 ± 0.1 eV is related to the C-OR bonds, the component peak centred at 288.6 \pm 0.1 eV corresponds to the O–C=O bonds and the component peak at the 291.5 \pm 0.1 eV is from the broad aromatic shake up. In Figure 6, the intensities of the aromatic carbon and C_H-H bonds in the C 1s spectra were nearly saturated at the IB exposure angles between 15° and 60° . This means that the bond breaking was activated in this range. Contrastingly, the phenomenon was weak at the IB exposure angle of 75° because the intensities of the bonds were relatively higher than those at the other intensities. We also observed the newly produced C=O bonds centred at 287.6 \pm 0.1 eV between the IB exposure angles of 30° and 60°, although the production was scant at 15° and 75°. That is, IB bombardment transformed carbon oxide bonds on the PS surfaces into C=O bonds in the direction of the anisotropic IB exposure process via surface oxidisation [22-24]. Although the breaking phenomena of aromatic carbon and C_H were noticeably detected, the produced C=O bonds strongly contributed to the LC alignment properties on the PS surfaces, because the error values of the measured tilt angles in Figure 2 were smallest at the IB exposure angle of 45°, which induced the greatest bond intensity. Additionally, the peaks with a peak near ~ 291.7 eV was easily broken at 45° . Therefore, the produced C=O and the selective bonding breaking could induce anisotropic dipole fields to align the LC molecules.

Figure 7 shows the core-level XPS spectra of O 1s. The component peak located at 531.9 ± 0.1 eV is due



Figure 5. (a) The measured contact angle values on IB-irradiated PS surfaces. (b) Images of the observed photographs of the contact angles.



Figure 6. The XPS spectra for the C 1s peaks of IB-irradiated PS surfaces as a function of IB exposure angle with an IB energy of 2 keV and an exposure time of 1 min.

to the O=C bonds. The high binding energy component peak centred at 534.7 \pm 0.1 eV is assumed to be due to surface contamination by surface trapping of methylene. The low binding energy component peak at 530.7 \pm 0.1 eV is due to the O–C bonds, which, along with O=C, are the important peaks. Generally, O-C and O=C bonds are the dominant peaks on PS surfaces; therefore, detecting only O-C bonds at the IB exposure angle of 75° confirmed that the bonds were broken in the direction of IB bombardment in the range from 15° to 60°. Observing the intensities of the O=C bonds as a function of the IB exposure angle, it was found that O=C bonds were easily broken in the range from 45° to 75° . The analysis shows that all of the O=C and O-C bonds could be broken at the IB exposure angle of 45°. Those results are strongly related to the stable LC alignment property, because the clearest LC alignment was produced at an angle of 45°. This means that IB irradiation for selective bond breaking could produce anisotropic dipole fields on PS surfaces.

Figure 8 shows the measured electro-optical (EO) characteristics, and the LCD transmittance curve for the IB-bombarded PS surface at an IB exposure angle of 45°. The curve was mostly clear and stable. Considering the threshold voltage of 2.242 V, the anchoring energy on IB-irradiated PS surfaces should be smaller than that on rubbed PI or PS surfaces. Although the threshold voltage could be affected by two factors, the anchoring energy [25] and the pretilt angle [26], the threshold voltage was hardly affected by the pretilt angle when the IB bombardment process was used in previous research [5]. Therefore, the anchoring energy is the main cause of the deviation of the threshold voltage between PS and PI.

4. Conclusions

In this study, it was determined that the homogeneous LC alignment property varied with IB exposure angle at fixed IB bombardment energy and time. The smallest error value was found at an IB exposure angle of 45°,



Figure 7. The XPS spectra for the O 1s peaks of IB-irradiated PS surfaces as a function of IB exposure angle with an IB energy of 2 keV and an exposure time of 1 min (colour version online).



Figure 8. Transmittance curve of the TN LCD on the IBirradiated PS surfaces as a function of applied AC voltage.

which produced clear LC alignment characteristics without any defects. Although IB bombardment might alter the physical properties of PS surfaces, the XPS spectra suggest that the chemical reaction caused by IB bombardment on a PS surface is the most likely cause of physical changes. XPS analysis also showed that the breaking of C_F bonds was confirmed to be a function of IB exposure angle. The breaking of $C_{\rm F}$ bonds and newly produced C=O bonding, however, was strongly related to the stable tilt angles of the homogeneous LC molecules, and the bonds were easily broken at an IB exposure angle of 45°. Moreover, O=C and O-C bonds were easily broken under the same IB exposure conditions. Measuring the contact angles on PS surfaces showed that the strongest anisotropic surface energy would be induced via IB exposure processing on PS surfaces at an angle of 45°. Finally, the measured EO characteristics of LCDs on IB-irradiated PS surfaces suggest that PS material compounded with methyl and fluorocarbon could replace PI material as the conventional LC alignment material.

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