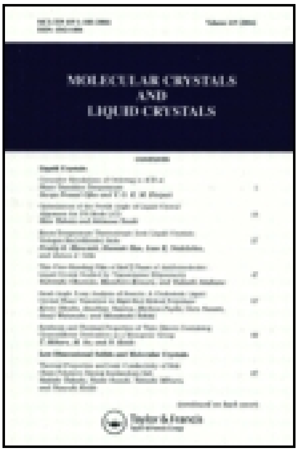

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Study on the Relation Between Rubbing Conditions and Physical Parameters of Polyimide

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Physical parameters on polyimide (PI) surfaces were investigated via spectroscopic techniques as a function of ROLLER ROTATION SPEED and STAGE MOVING SPEED of a rubbing process. The observed parameters exhibited the following trends; the parameters, such as anchoring energy and induced anisotropy, were enhanced as ROLLER ROTATION SPEED and STAGE MOVING SPEED increased until an optimal condition was reached. However, the parameters reversely degraded as those increased over optimal value of treating condition. From Raman spectroscopic measurements, we confirmed that strongly rubbing-treated PI over optimal condition was chemically degraded, resulting in degrading the parameters of PI.

Keywords Anchoring energy; liquid crystal; raman spectroscopic; rubbing condition; spectroscopic ellipsometer

1. Introduction

Various techniques have been developed for liquid crystal (LC) alignment, such as oblique evaporation of inorganics [1], photo alignment [2,3], Langmuir-Blodgett films [4], atomic force microscopy (AFM) [5,6], lithography of polymers [7], and the rubbing process [8]. Therefore, the studies on aligning LCs have been an active research topic over the past several decades. Recently, detailed studies at the molecular interaction level have been conducted via near-edge X-ray absorption fine structure (NEXAFS) [9], X-ray photoemission spectroscopy [10], second harmonic generation [11], photo-elastic modulation, AFM [5,6], contact angle [12], spectroscopic ellipsometer [13], etc.

In this work, we evaluated physical parameters such as the anchoring energy (AE) and induced anisotropy ($\Delta n_{induced}$) of polyimide (PI) surfaces for LC alignment as a function of ROLLER ROTATION SPEED and STAGE MOVING SPEED of

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rubbing process. Raman measurements were also performed to obtain information on bonding structure of the carbons in rubbing-treated PI.

2. Experimental Methods

Indium-tin-oxide (ITO) coated glass substrates were spin coated with PI (AL-60101, JSR), prebaked at 80°C for 30 min, and cured at 230°C for 1 h. The PI surfaces were rubbed along the y-axis direction, as shown in Figure 1. The roller used in this work was covered with a cotton velvet cloth (Agehara velvet). Rubbing depth was fixed at 0.1 mm. LC cells with a cell gap of 3.8 μm were fabricated using these rubbing-treated substrated, and a positive LC (Merck MLC-6608) was injected into the cells to evaluate the polar AE. The polar AE was determined by the capacitance-voltage (C-V) method. The method can be measured as a standard measure of this AE without additional numerical calculation. Especially, the C-V method was widely used to measure the AE on the LC alignment layers such as a rubbing-, photo-, and IB-treated surfaces, etc.

Variable angle spectroscopic ellipsometry (VASE) data for the rubbing-treated surfaces were acquired by using a VASE spectroscopic ellipsometer (J. A. Woollam) over the wavelengths of 400∼800 nm in increments of 10 nm for the anisotropy measurement. Ellipsometry was measured 21 times for each sample. Raman spectra were measured using a Raman microscope (Nanofinder 30, Tokyo Instruments Co.) with excitation at 488 nm in the backscattering configuration. We used a microscope with a 40 × objective lens immersed in water to minimize the sample damage. The laser power incident on the sample was less than 200 mV to avoid heating the substrate. The measurement was performed over wave numbers of 400∼3400 cm^{-1}.

3. Results and Discussion

3.1. *Dependence on ROLLER ROTATION SPEED*

First, we measured the AE of the rubbing-treated PI as a function of ROLLER ROTATION SPEED from 200 to 2000 r.p.m. Here, the stage speed of rubbing

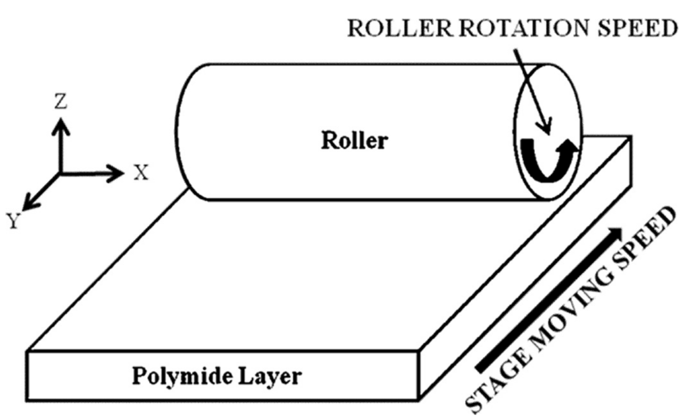

Figure 1. Experimental geometry of the rubbing-treated PI surfaces (rubbing direction: y-axis direction).

machine was fixed at 10 cm/s. When the ROTATION SPEED was treated over 200 r.p.m. on PI surfaces, LC molecules were able to be uniformly aligned. As depicted in Figure 2, the observed AE increased from 3.2 to 6.7×10^{-3} J/m^2 as the ROLLER ROTATION SPEED increased from 200 to 1200 r.p.m. However, the AE decreased from 6.7 to 0.4×10^{-3} J/m^2 as the ROLLER ROTATION SPEED increased from 1200 to 2000 r.p.m.

Next, we measured refractive index (n) spectra to observe the anisotropy of the PI surfaces as a function of ROLLER ROTATION SPEED via spectroscopic ellipsometry. The pure PI surface exhibited isotropic properties. However, after rubbing the PI surfaces at a certain ROLLER ROTATION SPEED, a discrepancy between the refractive index along the parallel to the rubbing direction direction (n_y) and along the perpendicular to the rubbing direction (n_x) was observed, which means that anisotropy was induced. The value of $\Delta n_{induced}$ ($=n_y$–n_x) increased with an increase in the ROLLER ROTATION SPEED in the range of 200$\sim$ 1200 r.p.m., (Figs. 3(a) and 3(b)). However, the value of $\Delta n_{induced}$ via the ROLLER ROTATION SPEED over 1400 r.p.m. was smaller than that of $\Delta n_{induced}$ via the ROLLER ROTATION SPEED at 1200 r.p.m., as shown in Figures 3(c) and 3(d). In other words, $\Delta n_{induced}$ increased until an optimal value of ROLLER ROTATION SPEED (i.e., 1200 r.p.m.) was reached. However, $\Delta n_{induced}$ reversed and decreased as rotation speed increased over the optimal ROLLER ROTATION SPEED.

In addition, we found that the n_x of the PI through higher ROLLER ROTATION SPEED exhibited less dependence on wavelength than that of the PI through lower ROLLER ROTATION SPEED (Figs. 3(c) and 3(d)). In general, the refractive index curve shifts toward lower wavelengths as the optical band gap energy increases. We calculated the value for the optical band gap energy of the rubbing-treated PI surfaces. For the PI through lower ROLLER ROTATION SPEED ($\leq$1200 r.p.m.), the optical band-gap energy was ca. 5.54 eV. However, for the PI through higher ROLLER ROTATION SPEED (1200$\sim$2000 r.p.m.), the

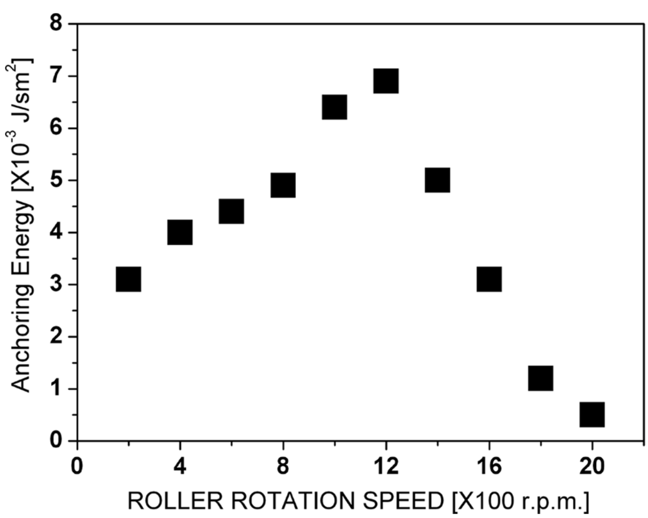

Figure 2. Observed AE as a function of ROLLER ROTATION SPEED.

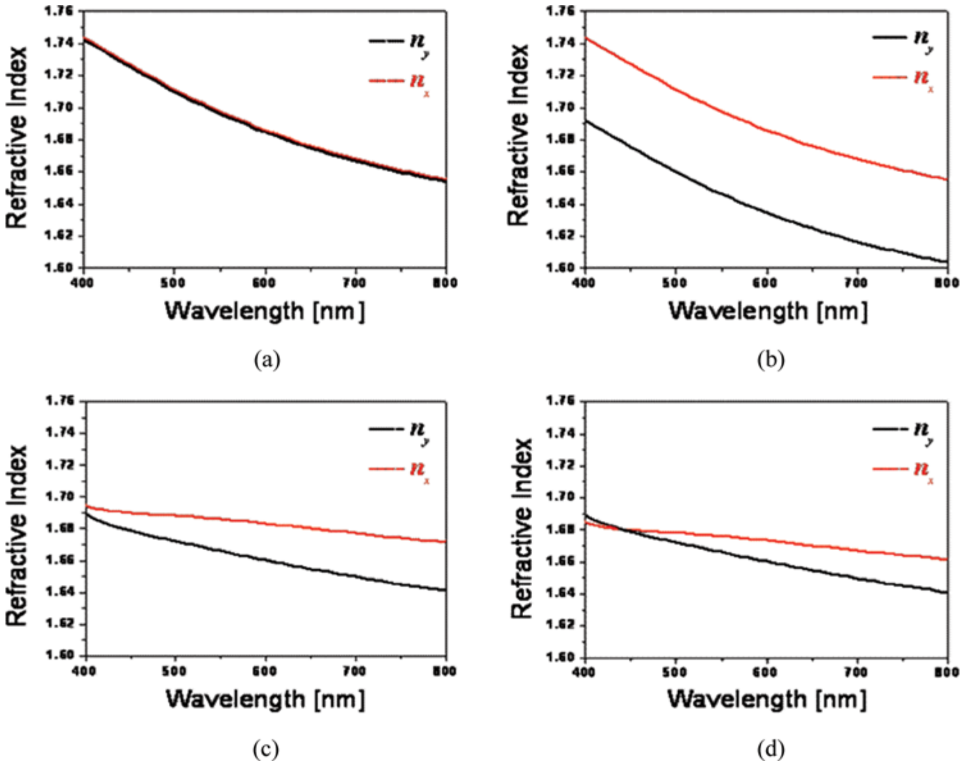

Figure 3. Detected n_y and n_x on PI surfaces via (a) 400, (b) 1200, (c) 1400, and (d) 1800 r.p.m. of ROLLER ROTATION SPEED. (Figure appears in color online.)

optical band gap energy was increased from roughly 5.54 to 6.28 eV. The increase can be explained by the increase in the amount of the hydrogenated amorphous carbon-like structure. The band gap energy of the PI through higher ROLLER ROTATION SPEED was higher than that of the PI through lower ROLLER ROTATION SPEED. Thus, the refractive index curve shifted toward lower wavelengths. Consequently, the refractive index of the PI through higher ROLLER ROTATION SPEED was less dependent on the wavelength than that of the PI through lower ROLLER ROTATION SPEED.

To determine why the characteristic trends critically changed before and after the optimal rotation speed condition, we performed Raman spectroscopic measurements which is a powerful tool for obtaining detailed information on the bonding structure of carbons [14]. Figure 4 shows the Raman spectra of PIs treated by several ROLLER ROTATION SPEEDs. As the rotation speed increased, two absorption peaks were slightly increased at 1366 and 1570 cm^{-1} in PI treated with rubbing process. These two peaks were due to the generation of a hydrogenated amorphous carbon-like structure [12]. Based on these observations, we conclude that the PI surface was chemically changed by rubbing process treatment, which ultimately resulted in degradation of the alignment characteristics of PI. In other words, we clearly confirmed that there is a close relation between the physical and chemical properties of rubbing-treated PIs.

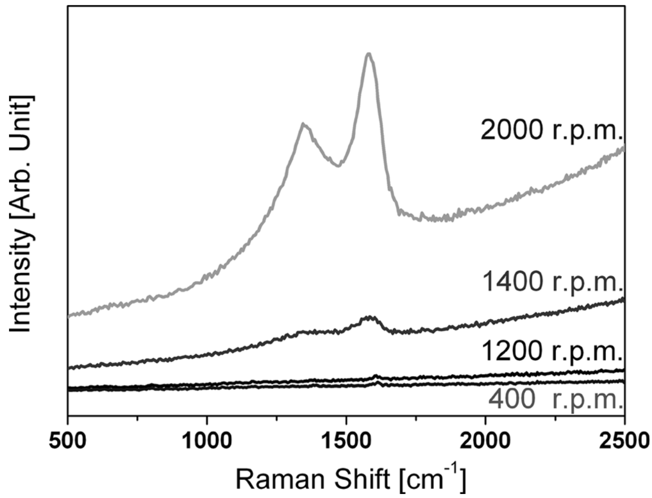

Figure 4. Raman spectra of rubbing-treated PI surfaces as a function of a ROLLER ROTATION SPEED.

3.2. *Dependence on STAGE MOVING SPEED*

We also checked the AE on the rubbing-treated PI as a function of STAGE MOVING SPEED from 2 to 18 cm/s. Here, the ROLLER ROTATION SPEED was fixed at 1200 r.p.m. When the STAGE SPEED was fixed over 2 cm/s on PI surfaces, LC molecules were able to be uniformly aligned. As depicted in Figure 5, the observed AE increased from 2 to $6.7 \times 10^{-3}\,\mathrm{J/m^2}$ as the STAGE MOVING SPEED increased from 2 to 10 cm/s. However, the AE decreased from 6.7 to $0.1 \times 10^{-3}\,\mathrm{J/m^2}$ as the STAGE MOVING SPEED increased from 10 to 16 cm/s.

We measured refractive index spectra to observe the anisotropy of the PI surfaces as a function of STAGE MOVING SPEED via spectroscopic ellipsometry.

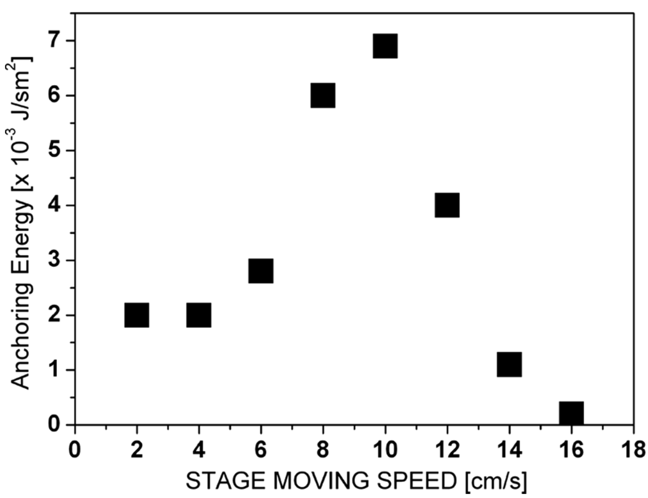

Figure 5. Observed AE as a function of STAGE MOVING SPEED.

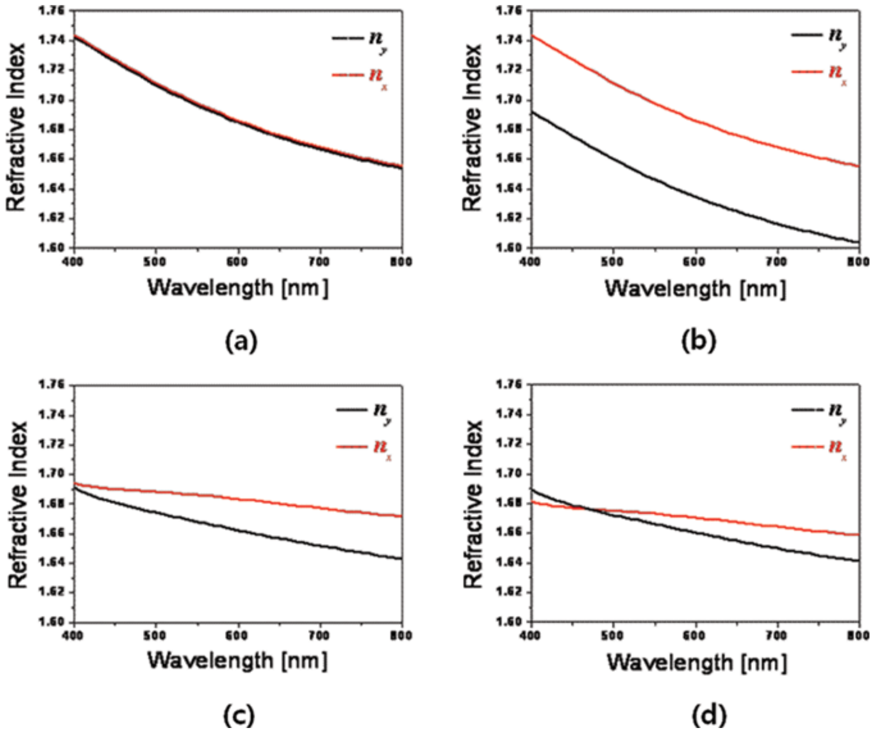

Figure 6. Detected n_y and n_x on PI surfaces via (a) 4, (b) 10, (c) 12, and (d) 16 cm/s of STAGE MOVING SPEED. (Figure appears in color online.)

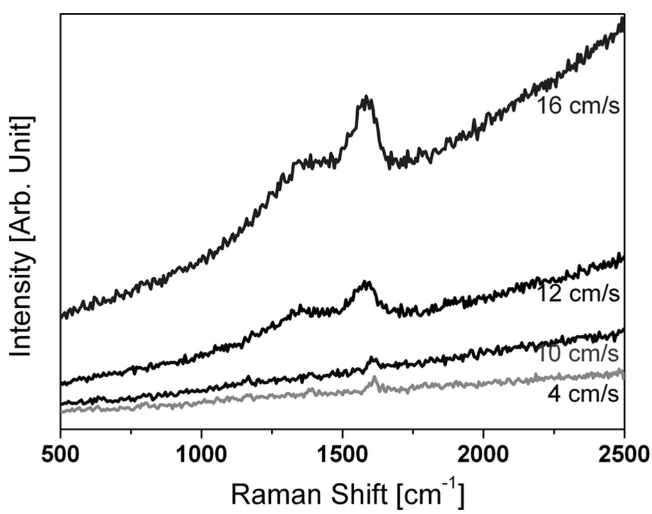

Figure 7. Raman spectra of rubbing-treated PI surfaces as a function of a STAGE MOVING SPEED.

The value of $\Delta n_{induced}$ increased with an increase in the STAGE MOVING SPEED in the range of 2~10 cm/s (Figs. 6(a) and 6(b)). However, the value of $\Delta n_{induced}$ via the STAGE SPEED over 12 cm/s reversed and was smaller than that of $n_{induced}$ via the STAGE MOVING SPEED at 10 cm/s, as shown in Figures 6(c) and 6(d). Namely, $\Delta n_{induced}$ increased until an optimal value of a certain condition (i.e., 10 cm/s) was reached. However, $\Delta n_{induced}$ reversed and decreased as STAGE MOVING SPEED increased over the optimal condition. It was also noted that the n_x on the PI through higher STAGE MOVING SPEED exhibited less dependence on wavelength than that of the PI through lower STAGE MOVING SPEED. (Figs. 6(c) and 6(d)).

Figure 7 shows the Raman spectra of PIs treated by several STAGE MOVING SPEEDs. As the STAGE MOVING SPEED increased, two absorption peaks were observed and slightly increased at 1366 and 1570 cm^{-1}. These two peaks were also due to the generation of a hydrogenated amorphous carbon-like structure, consequently resulted in degradation of the alignment characteristics of PI.

4. Conclusions

In conclusions, we evaluated the physical parameters (AE and $\Delta n_{induced}$) on PI surfaces as a function of ROLLER ROTATION SPEED and STAGE MOVING SPEED of rubbing process. The observed parameters exhibited the following trends; the parameters were enhanced as ROLLER ROTATION SPEED and STAGE MOVING SPEED increased until an optimal condition was reached. However, the parameters reversed and degraded as ROLLER ROTATION SPEED and STAGE MOVING SPEED increased over the optimal value. From Raman spectroscopic measurements, we confirmed that the strongly rubbed PIs over the optimal conditions for ROLLER ROTATION SPEED and STAGE MOVING SPEED were chemically degraded, consequently resulting in degrading the physical characteristics on PIs.

Acknowledgment

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