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Molecular reorientation of polyimide film induced by thermal nanoimprint lithography and liquid crystals alignment on it

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ABSTRACT

The molecular orientations of thermally imprinted polyimide (PI) films with different film thickness were investigated by the polarized Fourier-transform infrared spectroscopy (P-FTIR). The results illustrated the molecular orientation in the residual layers and the one in the higher-lines were different. The polymer main chains in the residual layers were perpendicular to the lines and parallel to the substrate. The polymer main chains in the higher-lines were aligned normal to the substrate and C=O bonds perpendicular to the main chain were aligned along the line direction. The orientation of liquid crystals on the alignment layer was investigated by atomic force microscopy (AFM) and polarized optical microscopy (POM). The results demonstrated imprinted PI film could be an alignment layer for liquid crystals.

1. Introduction

The molecular orientation of an alignment layer plays a critical role in the liquid crystal display (LCD) industry. The rubbing process was found to create microgrooves along the rubbing direction and also to align polymer main chain along the rubbing direction [1–6]. Recently, some researches have been reported that rubbed polyimide (PI) with side-chain induced the planar alignment of LC perpendicular to groove because of the perpendicular orientation of side-chain [7]. However, orientation of main chain of the alignment layer is still parallel to groove direction. How to get an alignment layer of which molecular main chain is perpendicular to the groove has not been reported.

Besides rubbing method, the other novel methods have been widely studied to fabricate microgrooves, such as photolithography [8,9], soft embossing [10,11], surface modification [12,13] and nanoimprint lithography (NIL) [14,15]. Molecular orientation of the alignment layer induced by these novel methods has been reported [8–16].

As a high-resolution, high-throughput, low-cost, non-conventional lithographic method, NIL has been proposed and demonstrated in various fields [16–18]. At present, the thermal embossing form of NIL has been widely investigated, which relies on a melt squeeze-flow process to transform a smooth polymer film into a patterned surface [19]. Since this squeeze-flow process generates stresses, the residual stresses in the polymer film are noticed [20–22]. Although the squeeze-flow process might form the different molecular orientations in the higher-lines and in the residual layers, as far as we known, it has not been investigated by any measurement.

Many researchers have used grazing-incidence X-ray diffraction (GIXD) to evaluate the molecular orientation on line-patterned polymer film induced by NIL [23,24]. However, GIXD is usually used for investigation of the crystal orientation and observation of the molecular orientation on the surface and near-surface. It is known that the PIs absent the large domains with three-dimensional positional order [25]. Therefore, polarized Fourier-transform infrared spectroscopy (P-FTIR) is more suitable to investigate the molecular orientation for the bulk PI film, which includes the crystalline segment orientation and amorphous segment orientation. In addition, only the IR light polarized parallel to the polarization direction of an IR active vibration is absorbed. Thus P-FTIR was also used to determine the orientation of the

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different functional groups leading to models for the molecular orientation within the films [6,7]. Scheme 1 shows the chemical structure of PI.

In this study, a simple method, which is carrying out NIL on PI pre-polymer then hard baking, was used to fabricate a line-patterned PI alignment layer. The molecular orientation of this alignment layer was investigated by a P-FTIR. The results proved the molecular main chains in the residual layers of line-patterned PI film are perpendicular to the lines direction and parallel to the substrate. On the other hand, in the higher-lines of line-patterned PI film, the molecular main chains are normal to the substrate and C═O bonds are aligned along the line direction. Consequently, by the method of carrying out annealing after NIL, a striped alignment layer was obtained. In this alignment layer, the molecular orientation in the residual layers and the one in the higher-lines are different.

2. Experimental section

2.1. Materials

Pyromellitic dianhydride (PMDA), Oxydianiline (ODA) and N-methyl-2-pyrrolidone (NMP) were purchased from Wako Chemicals Co., Osaka, Japan without any further purification before being used.

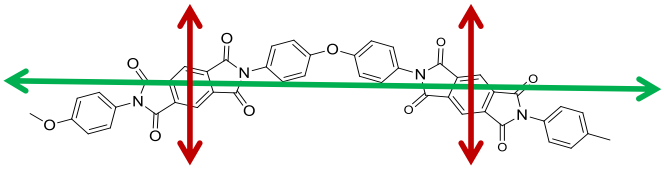
2.2. Preparation of poly(amic acid) (PAA) film

The PAA NMP solution was prepared by solution condensation polymerization at ambient temperature and at a concentration of 14.5 wt. % by solvent. After all PMDA (5.453 g, 0.0250 mol) was added increasingly to a stirred ODA (5.060 g, 0.0253 mol) NMP solution in an ice bath, the solution was stirred for 6 h without the ice bath. The solution was put into 3 °C refrigerator for all night and then it was recovered to room temperature naturally. An oil bath was used to heat the solution to 70 °C for 30 min. The PAA solution was sealed and stored in 3 °C refrigerator for using.

The PAA solution was diluted to a concentration of 10.91 wt. %, 5.45 wt. %, and 2.73 wt. % by NMP. The viscosity is 0.10 Pa s, 0.018 Pa s, and 0.011 Pa s, respectively. They were spin coated (90 s, 2500 rpm) on a Si wafer respectively. Soft-baking was carried out on a hot plate at 80 °C for 3 min before nanoimprint lithography.

2.3. Fabrication of nanoimprinting on PAA film

NIL was carried out on PAA film. A silicone mold bought from Kyodo International Inc. was used as a pattern master. To decrease the adhesion between the polymer and the mold, the silicone mold was treated with Optool DSX (Daikin Industries Ltd., 0.1 wt. % in Methoxy-nonafluorobutane [HFE7100]) for 1 min, rinsed by HFE7100, and dried under vacuum. The imprinting pressure was applied at 20 MPa and imprinting temperature is from 80 °C to 160 °C for 15 min. The hard baking of imprinted film was performed with a heating process from room temperature to 300 °C for 1 h and keeping at 300 °C for 1 h.



Scheme 1. Chemical structure of PI. The red and the green arrows show the direction of transition dipole moment vector for C═O asymmetric stretching vibration and C–O–C asymmetric stretching vibration respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.4. Preparation of alignment for LCs

The alignment of 4-n-pentyl-4″-cyano-p-terphenyl (5CT) was fabricated by depositing the droplets of 1 wt. % 5CT with tetrahydrofuran (THF) solvent on imprinted PI film. Self-assembly of 5CT was formed via THF solvent vapor annealing for 2 days.

2.5. Measurements

The morphology of imprinted PI films were investigated using S-4300SE (Hitachi Co., Ltd.) scanning electron microscope (SEM) at an accelerating voltage of 5 kV. A thin layer of osmium was coated on the sample surface before SEM observation.

The molecular orientation of imprinted PI film was investigated using a polarized micro-FTIR spectrometer (Auto IMAGE FTIR Microscope, PerkinElmer) in connection with autoimage microscope equipped with a mercury-cadmium telluride (MCT) detector. A polarizer which can be rotated by 360° was used during the measurement. Before sample measurement, the blank Si wafer was measured as a background. The spectra was analyzed by Spectrum, Version 5.0.1 software, copyright 2003 Perkin Elmer, Inc. Polar plots of the absorbance against polarization angles were generated by rotating the polarizer in 5° or 10° increments during the polarized IR measurements. The spectra were recorded with a resolution of 4 cm^{-1}, co-adding 32 scans. Aperture is 150 × 150 μm^2. The measurement was started after the equipment was stable. Baseline was corrected at the absorption of every peak before the polar plots was drawn.

Topography of aligned LCs on imprinted PI film was investigated by AFM (Pacific Nanotechnology, Inc., Nano-RTM) operating in close-contact mode. Silicon cantilevers with 225 μm length, 2.32 N/m spring constant and 73 KHz resonance frequency were used. Scanning rate was 0.1 Hz.

Polarized optical microscopy (POM) image of aligned LCs was observed at room temperature using a polarized microscope (Nikon Eclipse E400) in reflection mode.

3. Results and discussion

3.1. Morphology of imprinted PI film

Fig. 1 shows the SEM images of imprinted PI film after hard baking. The inset shows the cross sectional image. Line-width, groove-width, and line-height are ca. 650 ± 20 nm, 950 ± 20 nm,

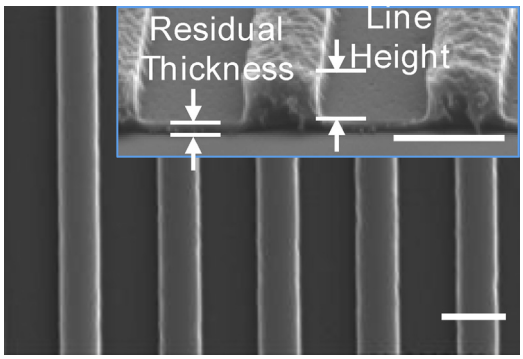


Fig. 1. SEM images of imprinted PI film. The inset shows the cross sectional view. (line-height: 570 ± 20 nm, residual thickness: 120 ± 20 nm) The scale bar is 1 μm.