

Characterization of Liquid Crystal Alignment on Rubbed Polyimide Film by Grazing-Incidence X-Ray Diffraction

The understanding of the alignment mechanism of liquid crystal (LC) on alignment film is of fundamental interest and of industrial importance in the manufacture of LC devices. Rubbed polyimide (PI) films have been used as liquid crystal alignment films in LC displays (LCDs). It is widely considered that molecules of liquid crystals are aligned by intermolecular interactions with PI molecules of rubbed films, and the characterization of polyimide molecular orientation is essential in the development and fabrication of LCDs. Until now, using grazing incidence X-ray diffraction (GIXD), which is a very powerful technique to characterize the molecular alignments of thin films, we have studied the effects of rubbing, washing and annealing on the surface structure of polyimide film [1].

In this study, we attempt to characterize the molecular alignment of a very thin liquid crystal layer (4 ~ 40 nm) formed on PI film to investigate the dependence of the molecular orientation of the LC film surface on the LC thickness to determine the interaction between LC and PI [2].

A nematic liquid crystal 4-pentyl-4'-biphenylcarbonitrile, denoted as 5CB, was used in this experiment. 5CB molecules are of rodlike shape and are aligned parallel to their molecular axes at room temperature. Poly (pyromellitic dianhydride oxydianiline), denoted as PMDA-ODA, was selected as the alignment PI film. A polyamic acid solution of PMDA-ODA was coated on Si substrates using a spinning coater. After pre-baking at 80°C for 5 min to dry the solvent, curing for imidization was performed at 250°C for 30 min. Then, PMDA-ODA films were rubbed under the condition that the insert depth of the fiber is 0.4 mm. The rotation and translation speeds of a rubbing roller were set at 300 rpm and 20 mm/s. The 5CB was evaporated executed under air atmosphere using an evaporation chamber. By heating the 5CBs at 100°C, the 5CBs are gradually evaporated onto the rubbed PMDA-ODA-coated substrate. The evaporation times were 5, 10, 20 and 40 min.

X-Ray reflectivity (XRR) and GIXD measurements were performed using the multi-axis diffractometer installed at beamline **BL19B2**. Scattered X-rays from samples were detected using a NaI scintillation counter through a Soller slit with a 0.089° divergent angle ("KeV" Co. Ltd.).

Figure 1 shows the observed X-ray reflectivity of the 5CB evaporated film onto the rubbed PMDA-ODA-coated substrate. The evaporation time was 10 min. The analysis was carried out by tuning both the mass

density and thickness of the PMDA-ODA and 5CB film to fit the observed reflectivity. The estimated film thicknesses of the PMDA-ODA and 5CB film were 100.9 and 8.9 nm, respectively. A linear relationship between the film thickness of the 5CB and evaporation time was observed as shown in the inset of Fig. 1.

In-plane φ - 2θ scans of the 5CB evaporated film of 38.4 nm thickness onto the rubbed PMDA-ODA film shown in Fig. 2(a) were obtained under the condition that the incident angle was set at 0.10°. Under this condition, we could obtain surface-sensitive information of the 5CB thin film. Blue and red solid circles indicate the observed in-plane φ - 2θ profiles whose scattering vector is parallel and normal, respectively, to the rubbing direction. Strong and somewhat broad diffraction peaks were clearly observed at around 16.0°. These diffraction peaks mainly come from the intermolecular correlation perpendicular to the molecular axis of the 5CB (Fig.3). The surface sensitive peak of the 5CB layer was stronger in the normal to rubbing direction. This means that the 5CB molecules preferentially aligned in the rubbing direction.

Figure 2(b) shows Bragg d-spacings of the 5CB's broad diffraction peaks at around 16.0° estimated by profile fitting. In addition, Bragg spacings in the normal (blue star) and parallel (red star) directions corresponded to the PI chain, and that of the 5CB directly deposited on the Si substrate without the rubbed PMDA/ODA film (green star) is indicated in Fig. 2(b). The larger Bragg spacing of the 5CB in

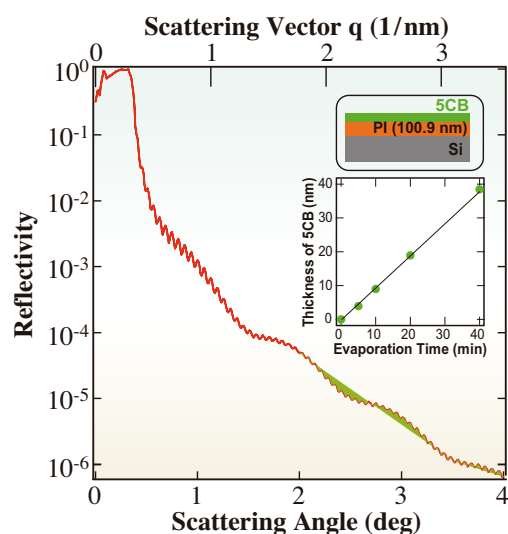


Fig. 1. Observed X-ray reflectivity of the 5CB film evaporated for 10 min onto the PMDA-ODA film. The inset shows the linear relationship between the 5CB film thickness and evaporation time.

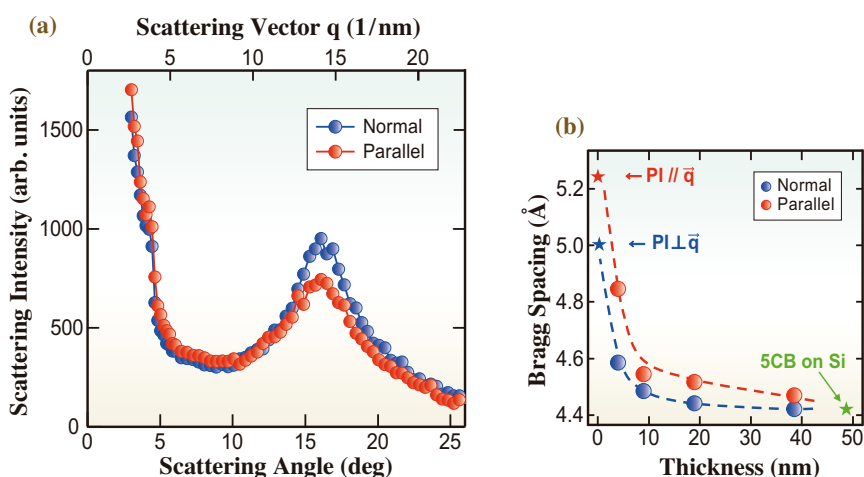


Fig. 2. (a) In-plane φ - 2θ profiles of the 5CB evaporated film onto the rubbed PMDA-ODA film. (b) Estimated Bragg spacing of the 5CB's broad diffraction peaks.

the parallel direction can be explained by considering that 5CB molecules were strongly bounded by PI chains in the parallel direction with longer interchain spacings. The estimated Bragg spacings in both directions decrease with increasing 5CB film thickness, and seem to approach that of the 5CB film directly deposited on the Si substrate. In the 5CB films thinner than 10 nm, their estimated Bragg spacings seem to asymptotically increase to those of rubbed polyimide film in the parallel and normal directions with decreasing thickness of the 5CB film to zero. The behaviors of the 5CB films described above suggest that the 5CB molecules are strongly bounded by the rubbed polyimide film, and that the 5CB molecules have similar periodicity to the rubbed PI at the interface of PI. As the distance from the alignment film increases, the effect of the alignment film becomes weaker and the intermolecular spacing of the 5CB comes close to the intrinsic intermolecular

spacing. It was also observed that the peak width at around 16° decreases with its thickness, which is considered to indicate the lower 5CB ordering near the rubbed polyimide film (Fig. 3).

In summary, we characterized the molecular distribution in a very thin liquid crystal layer evaporated onto rubbed polyimide film. The anisotropic distribution of liquid crystal molecules in the thin 5CB layer was successfully observed by GIXD. In the surface-sensitive in-plane diffraction, we found that the 5CB film thickness affects the Bragg spacing and ordering, which were estimated from the diffraction peak position and width. In the vicinity of the alignment film, the intermolecular spacing of the 5CB is expanded by the alignment film in the direction perpendicular to the molecular axis of the 5CB molecule. It was also proved that the 5CB is less ordered near the PI film. The intermolecular spacing of the 5CB becomes close to its intrinsic value as it recedes from the PI film.

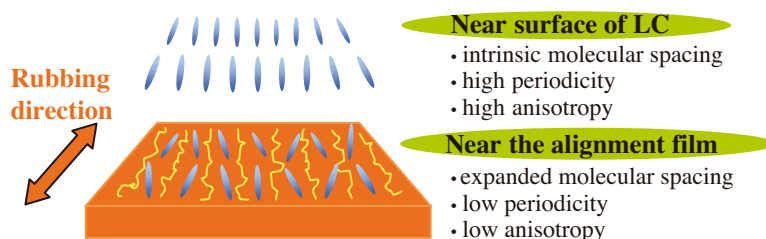


Fig. 3. Illustration of proposed model for the 5CB molecular alignment. The blue arrow indicates the intermolecular correlation perpendicular to the 5CB molecular axis.

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References

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