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Photo-induced in-plane alignments of nematic liquid crystal (LC) molecules, 5CB, have been investigated in the cell with alternate self-assembly films of polyelectrolyte and low-molecular weight dyes on the gold electrodes using the attenuated total reflection (ATR) measurement method. Reflectivities due to the excitations of the surface plasmon polariton (SPP) were observed in the ATR properties of the LC cell. In-plane switching of LC molecules adjacent to the aligning layer was evaluated from the ATR curves by means of irradiation of the linearly polarized visible light to the LC cell. It was also estimated that the re-orientation of the LC molecules occurred within about 130 nm from the surface of the aligning layer on the prism by the irradiation of the polarized light.

Keywords: ATR; nematic liquid crystal; photo-induced in-plane alignment; alternate self-assembly film; SPP

1. INTRODUCTION

Evaluation of behaviors of liquid crystal (LC) molecules in cells is very important in order to control orientations of LC molecules and to develop cells having new photo-aligning layers. Recently attenuated total reflection (ATR) measurements [1] have been used for evaluations of LC molecules in cells[2-4]. The tilt angles of LC molecules close to the surfaces of aligning layers and in a whole cell can be estimated from the surface plasmon polariton (SPP) [5] and the guided wave excitation modes (GWEM) [6], respectively [7]. However, an evaluation of in-plane orientations of LC molecules utilizing ATR measurement has been rarely reported until now [8].

Self-assembly films are of great interest because the ultrathin molecular films can be easily obtained by means of alternate polyelectrolyte depositions of molecular anions and cations. Recently, fabrications of self-assembly films from polyelectrolyte and low-molecular weight azo dyes have been reported [9]. The incorporation of a photochromic moiety in the ultrathin film is very attractive because of the possibility of new light-sensitive films and optical devices. Self-assembly films containing photoisomerizable azo dyes are hoped to be aligning layers to control LC molecules by irradiation of light [10].

In this report, photo-induced in-plane alignments of nematic liquid crystal (LC) molecules, 5CB, have been investigated in the cell with alternate Direct Red 80 (DR80)/poly(diallyldimethylammonium chloride) (PDADMAC) self-assembly films [11] on the gold electrodes using the ATR measurement method. From the ATR curves, in-plane switching properties of the LC molecules and the orientations in the LC cell were evaluated during and after the irradiation of linearly polarized light.

2. EXPERIMENTAL DETAILS

Figure 1 shows the Kretschmann configuration for the ATR measurements, the LC cell and the molecular structures of the polyion (PDADMAC) and the azo dye (DR80) used in the experiments.

The half-cylindrical prisms (HOYA FDS90, n=1.85) were used for the ATR measurements. Gold films approximately 40 nm thick were evaporated onto the flat side of the prisms. After surfaces of the prisms with gold films and slide glasses were functionalized with 3-aminopropyltiethoxysilane, the layer-by-layer adsorptions of the DR80/PDADMAC self-assembly films were performed as follows: the molecular layers of the PDADMAC and the DR80 were alternately deposited from these aqueous solutions with 0.01 M on the coated prisms and slide glasses as the aligning layers of the LC cell. These self-assembly films had 5 bilayers on the coated prisms and 100 bilayers on the slide glasses. Each deposition on these substrates was carried out for 15 minutes including the immersion and a rinsing step

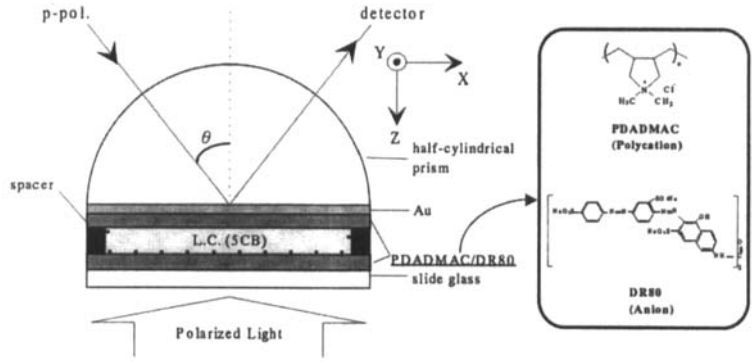

FIGURE 1 The Kretschmann configuration for the ATR measurements, the LC cell and the molecular structures.

in deionized water.

The alignment layers of the DR80/PDADMAC films on the prism were irradiated with linearly polarized visible light before fabricating the LC cell. A high dichroism of the DR80/PDADMAC films due to the n-π^* transition of azobenzene dyes (DR80) by the irradiation has been observed in our previous report [12]. Reflectivities in the ATR experiments were measured for the LC cell as a function of the incident angles of a He-Ne laser at 632.8 nm, or at the resonant incident angle of the SPP during the irradiation of the linearly polarized visible light to the cell through the slide glass without the former irradiation as shown in Fig. 1. The nematic liquid crystal was 4-cyano-4'-n-pentylbiphenyl (5CB: Merck Japan co.). Reflectivities in the GWEM were also measured as a function of the incident angle of the laser in a similar system without Au thin film on the prism. The slide glasses with arachidic acid for the homeotropic alignment of the LC molecules were used in the GWEM measurement.

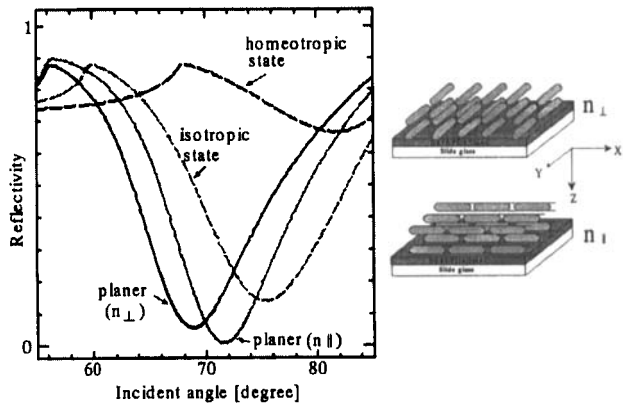

Figure 2 Calculated ATR curves of the LC cell

Furthermore, the complex dielectric constants and the thicknesses of the gold films on the prisms and the DR80/PDADMAC films were determined from the ATR measurements using another type of prism (BK 7, n = 1.515) before the ATR measurements of the LC cells.

Figure 2 shows the calculated ATR curves for the four idealized cases due to the excitation of the SPP, assuming that the tilt angles of the nematic LC molecules, 5CB, are uniform and the cell has a semi-infinite thickness. The theoretical ATR curves were calculated using a transfer matrix method [13]. In the calculations, the refractive index of the LC molecules was used from a literature [14]. Large valleys in the reflectivities of the ATR curves are caused by the resonant excitations of the SPP. The calculated ATR properties are shown in the two planer alignments, where the long axes of 5CB molecules is parallel to the plane of the incident laser beam and the other is vertical that have the refractive indexes of $n_{\parallel}$ and $n_{\perp}$ in the plane, respectively. If the azimuthal tilt angles of the LC molecules of the planer alignments change from vertical to parallel, the ATR properties sensitively move to the higher region in the incident angle as the refractive indexes, i.e. the dielectric constants increase from $n_{\perp}$ to $n_{\parallel}$. The refractive index of the isotropic state is assumed to be the average of these, i.e., $n_{iso}=n_{ave}=[(1/3)(n_{\parallel}^2 + 2n_{\perp}^2)]^{1/2}$ [8].

3. RESULTS AND DISCUSSION

ATR properties of the liquid crystal cell

Figure 3(a) shows the experimental ATR curves in the region of the resonant angles of the SPP for the LC cell. The experimental procedure was as follows: Line 1 was measured before the irradiation of the visible light, Line 2 after 1-hour irradiation of the polarized

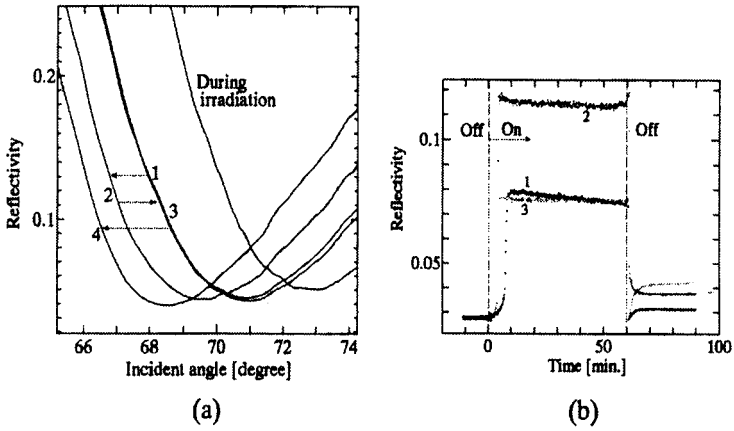

Figure 3 ATR curves of the LC cell (a) and Reflectivity change of the ATR during irradiation at the excited angle of the SPP (b).

visible light, parallel to the x-direction as shown in Fig. 1, Line 3 after 1-hour irradiation of the polarized visible light, parallel to the y-direction and Line 4 after 1-hour re-irradiation of the polarized light, parallel to the x-direction. The results show that the ATR measurements are very sensitive to the irradiation of the linearly polarized visible light, which depend upon orientations of the LC molecules in the cell. The resonant angles of the SPP, the angles at the minimum of the reflectivities, decreased with the irradiation of the polarized visible light in the x-direction, and increased with the irradiation of the polarized visible light in the y-direction. From the theoretical ATR curves as shown in Fig. 2, the shifts of the resonant angles to the lower angles as a result of irradiation of the polarized visible light in the x-direction indicated that the in-plane alignment of LC molecules within the penetration length of the SPP was changed to the y-direction. Since the DR80/PDADMAC film on the prism side

was irradiated by the polarized visible light in the x-direction before assembling the cell, it was estimated that the alignment direction of the DR80/PDAMAC film on the slide glass resulted in the in-plane alignment of LC molecules within penetration depth of the SPP from the prism side. The shifts of the resonant angles to the higher angles as a result of the irradiation of the polarized visible light in the y-direction also indicated that the in-plane re-orientation of the LC molecules was changed to the x-direction. These properties showed that LC molecules on the DR80/PDADMAC film were aligned to the in-plane orientation perpendicular to the linearly polarized direction of the irradiation light.

Figure 3(b) shows the reflectivity changes of the ATR curves at the excited angle of the SPP as a function of the time during the irradiation of the linearly polarized light. It was clearly observed that the reflectivities were changed by the irradiation and the stop of the polarized light. The LC cell was kept about 25°C before and after the irradiation of the light, and kept about 40°C during the irradiation. In this measurement, the phases of the LC molecules near the aligning layers changed gradually after turning on and off the irradiation light, i.e., switching from the nematic state to the isotropic state of LC molecules and from the isotropic state to the nematic state, respectively. On the other hand, in the ATR measurements utilizing the GWEM measurements in the similar system, the phases of the LC molecules in the whole cell changed directly after turning on and off the irradiation light. From these ATR measurements utilizing the SPP and the GWEM, it was estimated that the switching behaviors of LC molecules from the nematic state to the isotropic state and from the isotropic state to the nematic state were different between the region near the aligning layer and the bulk region in the cell.

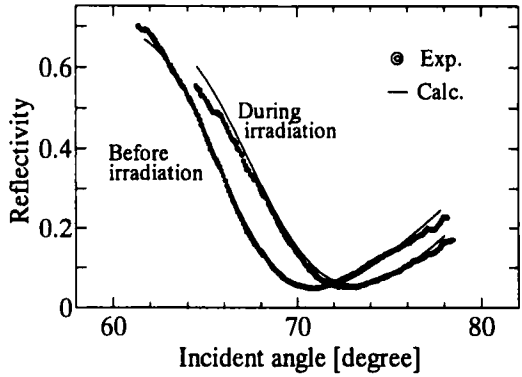

Figure 4 The experimental ATR curves of the LC cell and the calculated one.

Evaluation of the alignments of LC molecules

The LC cell was kept at about 40°C during the irradiation of the linearly polarized visible light. Therefore, assuming that the LC molecules, 5CB, in the cell were an isotropic state, the theoretical curves were fitted to the experimental ATR curves during the irradiation. The calculations were carried out in the prism/Au/(DR80/PDADMAC)/LC system, assuming that the thickness of the LC layer was semi-infinite. The theoretical values due to the SPP excitation agreed with the experimental curves as shown in Fig. 4. The ATR curve before the irradiation was calculated assuming that the direction of the in-plane alignment was parallel to the y-direction, and the tilt angle was 33°. The calculation showed that the SPP penetrated from the surface of the aligning layer on the prism to about 130 nm in the LC layer. Therefore, it was estimated that the re-orientation of the LC molecules occurred within about 130 nm from the surface of the aligning layer on the prism by the irradiation of the

polarized light.

4. CONCLUSIONS

Photo-induced in-plane alignments of LC molecules were evaluated in the cell with new rubbing-free aligning layer of alternate DR80/PDADMAC self-assembly films on the gold electrodes using the ATR measurement method. The ATR properties due to the excitation of the SPP were observed. The properties were sensitively changed by re-orientations of the LC molecules by means of the irradiation of the linearly polarized visible light. The alignments of LC molecules were estimated by fitting the theoretical ATR curves to the experimental ones. It was also estimated that the re-orientation of the LC molecules occurred within about 130 nm from the surface of the aligning layer on the prism by the irradiation of the polarized light.

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