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Measurement of Tilt Angle of Nematic Liquid Crystal Near the Surface of Rubbed Polyimide by Means of the ATR Method

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An attenuated total reflection (ATR) method has been used to measure the changes of the average tilt angle of nematic liquid crystals near the surface of alignment film under the application of an electric field. The response of molecular alignment, in the region of about 140 nm from the liquid crystal/alignment film interface, upon the applied voltage, was obtained by this experiment. The results show that the average tilt angle near the interface increases monotonically with the applied field and tends to saturate to be 35° when an adequate field is applied up to 80 volts; this saturated value is small compared with the tilt angle at the mid-plane which is 90° . This behavior is well explained numerically in terms of elastic theory by assuming strong surface anchoring.

Keywords: Attenuated total reflection, nematic liquid crystal, metal plasmon surface electromagnetic wave

1. INTRODUCTION

For preparing liquid crystal sample cells or liquid crystal display (LCD) devices, it is necessary to control the LC surface alignment. For obtaining planar LC alignment accompanying the pretilt angle, rubbed polyimide films are commonly used¹ as aligning layers. Research and development of new LC alignment technology such as nonrubbing techniques and research on the characterization of the aligned phase of LC are being actively conducted by many workers.²

For characterizing the aligned phase of LCs, the following several methods are commonly utilized: observation of texture with a polarizing microscope, measurement of anchoring energy, measurement of pretilt angle, and so forth. These characterizations are made by observing or measuring the phenomenon occurring in the bulk region of a sample cell.

Recently several new methods, such as optical second harmonic generation³ or the attenuated total reflection method^{4,5} have been applied with the aim of understanding the phenomenon occurring in the interfacial region.

The present research has been conducted in order to understand the change of nematic (*N*) LC conformation in the interfacial region as a function of applied electric voltage and to measure the surface pretilt angle using the attenuated total reflection

method where NLC (5CB) is aligned, in particular, on the rubbed polyimide films that are capable of generating a high pretilt angle around 7 degrees.

2. PRINCIPLES

The system adopted in this research is called the Kretschmann scheme⁶ that comprises a prism coupler and a stacked multilayer which consists of an Ag metal film, rubbed polyimide alignment layers, and an ITO-coated glass substrate; in between an NLC is filled as shown in Figure 1. In this system a metal plasmon surface electromagnetic wave (MPSEW)⁷ is excited and this wave propagates along the interface of the Ag foil/polymer. We observe the reflectivity of a laser beam (TM mode) reflecting from the system as a function of incident angle θ_i in the prism. When the reflectivity shows a minimum at a particular θ_i , a MPSEW is excited. As a non-radiative wave, the optical field decays exponentially along the depth from the interfaces of Ag foil ϵ_m /polymer ϵ_{po} /LC layer ϵ_{LC} . Figure 2 depicts a schematic profile of the electromagnetic field as a function of depth z . The magnetic fields of the MPSEW in each region are written as follows: for Ag foil,

$$H_{ym} = H_m \exp(-K_{zm} z) \exp[j(\omega t - K_x x)]; \quad (1a)$$

for polymer film,

$$H_{ypo} = [H_{po1} \exp(-K_{zpo} z) + H_{po2} \exp(K_{zpo} z)] \exp[j(\omega t - K_x x)]; \quad (1b)$$

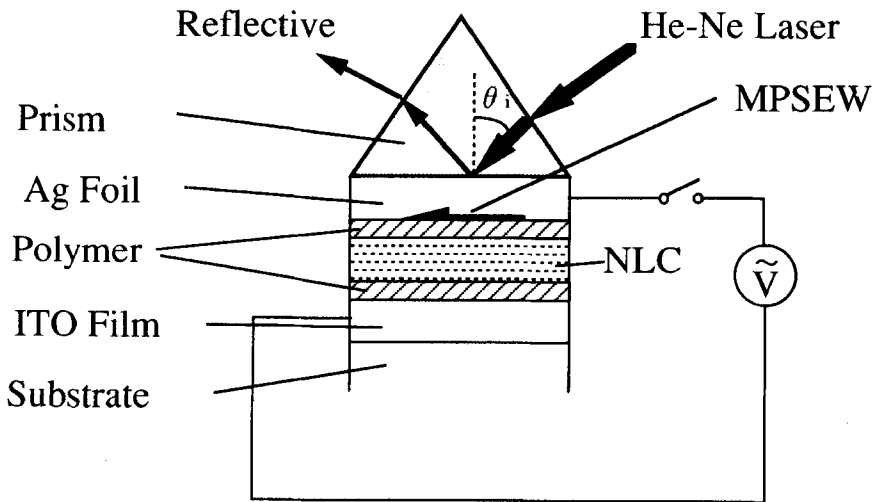


FIGURE 1 The MPSEW measurement experiment. By changing the p -polarized wave (TM mode) incident angle, the MPSEW propagating in the interfaces was excited. For Fredericks transition, the LC molecules were turned by applied electric force and different attenuated total reflection angles were observed.

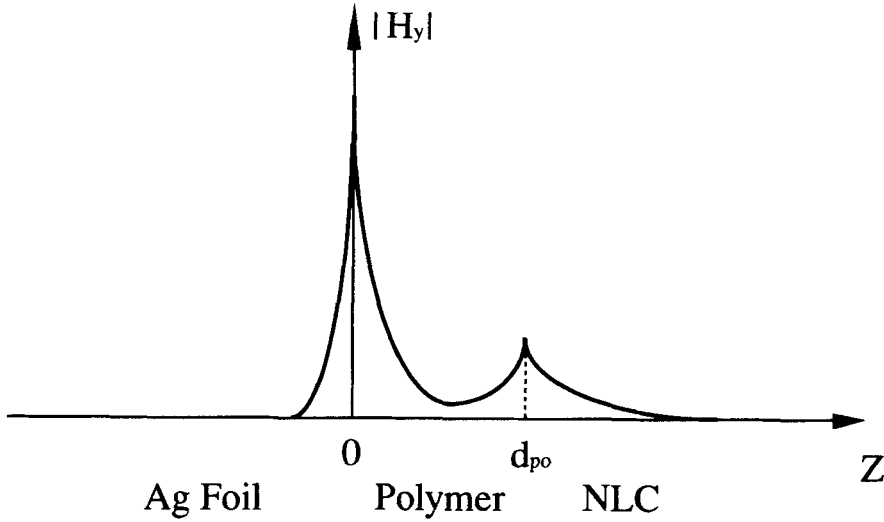


FIGURE 2 As there is a non-radiative surface electromagnetic field, the MPSEW propagates along the interfaces and decays exponentially and perpendicularly from the interfaces of the layers.

and for LC layer,

$$H_{yLC} = H_{LC} \exp(K_{zLC} z) \exp[j(\omega t - K_x x)]. \quad (1c)$$

Using the boundary conditions for the continual electromagnetic field, the eigenvalue equation of the MPSEW for this alignment state for the p -polarized field is obtained as,

$$(\varepsilon_{po} K_{zm} + \varepsilon_m K_{zpo})(\varepsilon_{LC} K_{zpo} + \varepsilon_{po} K_{zLC}) + (\varepsilon_{po} K_{zm} - \varepsilon_m K_{zpo})(\varepsilon_{LC} K_{zpo} - \varepsilon_{po} K_{zLC}) \exp(2K_{zpo} d_{po}) = 0 \quad (2)$$

with

$$K_{zi} = (K_x^2 - \varepsilon_i)^{1/2} \quad i = m, po, LC; \quad (3)$$

where the suffix i is for metal, polymer, and liquid crystal. The tangential component of the wave vector K_x reads

$$K_x = (\omega/c) n_p \sin \theta_i. \quad (4)$$

If the dispersion relation is fulfilled by changing the incident angle θ_i , the amplitude of the plasmon density oscillations increases and produces a strong electromagnetic field at the interface at Ag foil/polymer. The refractive index of NLC $n_{LC} = \varepsilon_{LC}^{1/2}$ in Equation (2) is an average in the region where the MPSEW shows $1/e$ decay in the interfacial region.

When an electric field is applied to the sample, the tilt angle θ_i of NLC will change and hence the refractive index of the light wave changes according to

$$n_{LC} = n_e n_o (n_e^2 \cos^2 \theta_i + n_o^2 \sin^2 \theta_i)^{-1/2}, \quad (5)$$

where n_e and n_o are the refractive indices parallel and perpendicular to the molecular axis, respectively. Once we obtain the n_{LC} from the measurement, then the θ_i can be determined with the help of Equation (5).

3. EXPERIMENT AND RESULTS

The attenuated total reflection is, in fact, a kind of energy conversion. For exciting the metal surface electromagnetic wave, the evanescent wave is produced below the bottom of the prism in the multilayer of Figure 1. When the tangential component of the wave vector of the incident wave is equal to the wave vector of the surface electromagnetic wave, the reflectivity falls to exhibit a minimum. It means that the energy of the incident wave is converted to the energy of a surface plasmon oscillation, and the surface electromagnetic wave is generated in the interface of the multilayer. As there is a very large negative real part of dielectric constant of the metal, the electromagnetic field intensity is very strong at its surface. But, as the prism is a coupler of the surface electromagnetic wave, the evanescent light wave radiates from the prism/metal interface. Therefore, as shown in Figure 2, the electromagnetic field intensity is strongest in metal/polymer interface, and also strong in the interface of polymer/LC, and decays slowly toward the deep direction of the LC layer.

In practice, the actual structure of our ATR system is as follows: on the surface of the prism (HOYA glass SF6, $n = 1.80489$ at 632.8 nm wavelength of He-Ne laser) an Ag foil of 100 nm thickness was evaporated in a vacuum system and a polyimide (PI) (Nissan Chem. Ind, RN-626, $n_{po} = 1.60$) alignment film is coated with a spinner on the Ag film (the thickness of PI films was measured by the ATR method and it was about 30 nm); and the second PI film covers the ITO-coated glass substrate; the PI films were rubbed in an antiparallel direction; a gap of 5 μm thickness was filled with NLC (5CB, $n_o = 1.5297$, $n_e = 1.7051$ at 632.8 nm wavelength He-Ne laser at 26°C, Merck Ltd.). an electric field is applied across the Ag film and the ITO film.

The reflectivity for a He-Ne laser light beam was observed by varying the incident angle θ_i . As θ_i increases the reflected wave intensity first increases and shows a maximum where a critical total reflection occurs and a reflectivity minimum is shown, the MPSEW is generated, as shown in Figure 3. From the observed incident angle giving rise to the maximum attenuation, the dielectric constant of the medium near the surface can be calculated by the MPSEW eigenvalue Equation (2), and thus we are able to calculate the pretilt angle from Equation (5).

For the quiescent condition, where $V = 0$, the observed minimum occurs at $\theta_i = 69.4^\circ$. This corresponds to the surface pretilt angle of 9.6° . As the applied voltage increases the observed value of θ_i , giving a reflection minimum also increases. In Figure 5, the applied voltage dependence of the pretilt angle is expressed by dots. The tilt angle increases rapidly up to 30° when $V = 20$ volts and then tends

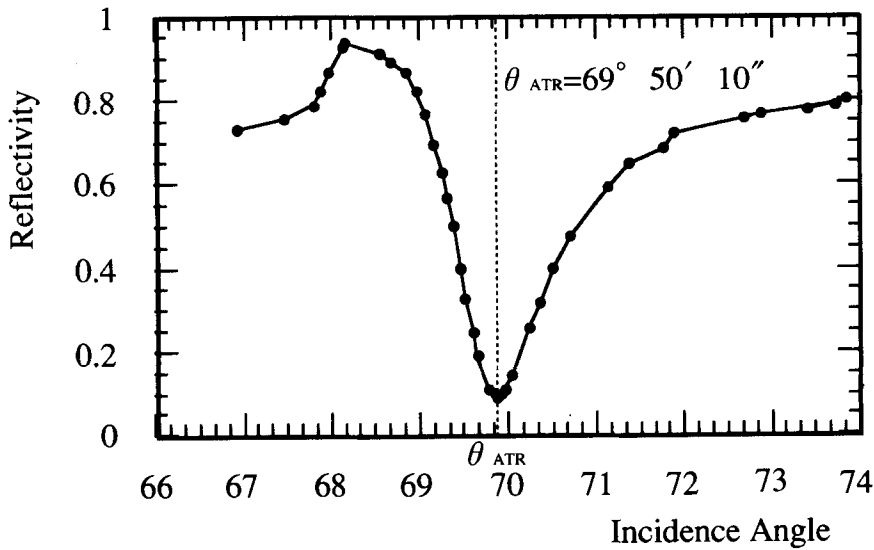


FIGURE 3 When there is a *p*-polarization incident wave (TM mode), the reflectivity was measured as a function of different incident angles in prism.

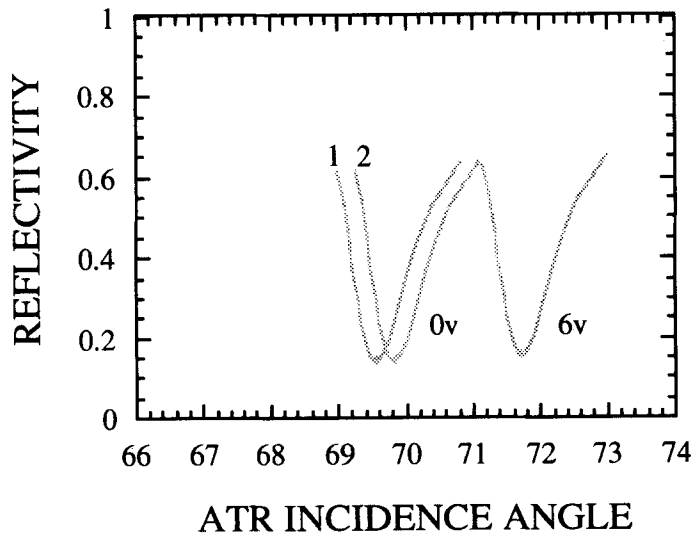


FIGURE 4 The attenuated total reflection angles in different applied voltages: curve 1: assume the pretilt angle = 0; curve 2: the sample cell applied voltage = 0 V; curve 3: the applied voltage = 6 V.

to saturate to 35° for 80 volts, where the tilt angle at the mid-plane is 90° for the applied voltage of 8 volts.

For verifying the results, we conducted a theoretical calculation based on liquid crystals elastic theory.^{8,9} The changes of tilt angle $\theta(z)$ as a function of distance z in the

direction of thickness for different applied voltages can be calculated by solving the equation:

$$\left(\frac{d\theta(z)}{dz}\right)^2 = \frac{\Delta\epsilon D^2}{K_{11}\epsilon_{\perp}^2} \frac{1}{1 + a \sin^2 \theta_m} \frac{1}{H^2(\theta(z))}, \quad (6)$$

where

$$H^2(\theta(z)) = \frac{(1 + a \sin^2 \theta(z))(1 + k \sin^2 \theta(z))}{\sin^2 \theta_m - \sin^2 \theta(z)},$$

$$a = \frac{\Delta\epsilon}{\epsilon_{\perp}}, \quad \text{and} \quad k = \frac{K_{33} - K_{11}}{K_{11}}.$$

The applied voltage is

$$v = \int_0^d \frac{D}{\epsilon_{\perp}(1 + a \sin^2 \theta(z))} dz \quad (7)$$

Because the electromagnetic field near the surface decays exponentially in a deep direction of the cell, it must be considered in the calculation of the average value of the tilt angle in the region at a distance t from LC/polymer interface. Therefore the average

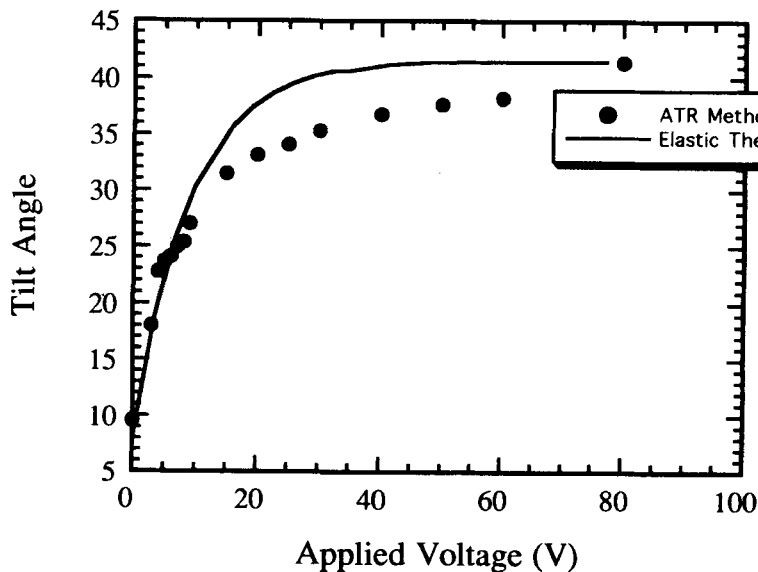


FIGURE 5 The relations of $\theta_i(V)$, by means of both the ATR method and elastic theory, when the pretilt angle is 0 and the surface anchoring energy is infinite. When the electric field goes over 20 V the tilt angle of NLC will go to 35° at the surface. Point: ATR method; curve: elastic theory.

value of tilt angle in this region could be calculated approximately by

$$\theta_{av} = \int_0^t \frac{\exp(-A k z) \theta(z)}{t} dz \quad (8)$$

$$k = k_0 (n_p^2 \sin^2 \theta_p - \varepsilon_{LC}(z))^{1/2} \quad (9)$$

where the $\exp(-A k z)$ is the evanescent wave decay relative function, k is the wave decay constant in LC, A is the evanescent wave relative constant. The solid line shown in Figure 5 indicates the calculated value using Equation (6) through Equation (9), where strong anchoring is assumed. A fairly good agreement between the experimental values and theoretical calculation is attained.

4. CONCLUSION

For an investigation of the surface pretilt angle and the applied voltage dependence of the tilt angle in the interfacial region of NLC (5CB) surface, a measurement of ATR has been made, where the NLC is aligned on rubbed polyimide films. First, the surface pretilt angle is determined to be 9.6° in this particular system; and second, the applied voltage dependence of the average tilt angle in the interfacial region (about 140 nm thick) is shown to increase up to 35° at the voltage where the tilt angle at the mid-plane is 90° already; this behavior is shown to agree with the theoretical calculation using the continuum theory and assuming strong anchoring.

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