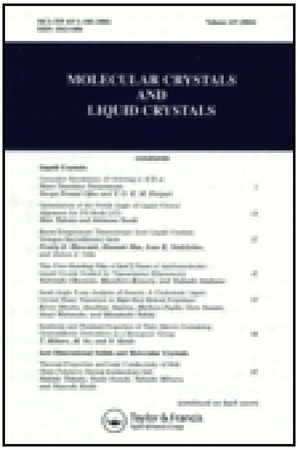

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Attenuated Total Reflection Properties and Complex Dielectric Constants in Azobenzene LB Films Adsorbing Cyanine Dyes

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Attenuated Total Reflection Properties and Complex Dielectric Constants in Azobenzene LB Films Adsorbing Cyanine Dyes

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Attenuated total reflection (ATR) properties have been investigated for azobenzene LB films adsorbing cyanine dyes on aluminum thin films. The ATR properties changed as the LB films were annealed. From the ATR properties, the complex dielectric constants were calculated as a uniaxial anisotropic dielectrics. It was thought that the ATR properties and the dielectric constants were caused by the dispersion properties due to the absorption bands.

Keywords: azobenzene LB film; cyanine dye; ATR method; uniaxial anisotropy; anomalous dispersion

INTRODUCTION

Azobenzene (Az) LB films adsorbing cyanine (Cy) dyes were expected to exhibit characteristics of each molecule and some interactions with these molecules [1]. As Az exhibits a cis-trans transition caused by photoisomerization and Cy is one of photosensitizing dyes, these molecules and the complex structure are of great interest in optical and electrical applications [1]. Attenuated total reflection (ATR) method [2] is one of useful techniques that can accurately estimate optical and/or dielectric properties and structures of ultrathin films such as LB films on metal thin films. In this paper, the complex dielectric constants were investigated for the Az LB films adsorbing the Cy dyes on aluminum (Al) thin films using the ATR measurements.

EXPERIMENTAL DETAILS

Figure 1 shows the chemical structures of the molecules used in this work. Cyanine dye (purchased from Japanese Research Institute for Photosensitizing Dyes Co.) and azobenzene (purchased from Dojindo laboratories) were used. Six monolayers of the Y-type Az LB films adsorbing the Cy dyes were deposited on the evaporated Al thin films covered with the cadmium arachidate salt LB monolayer. Figure 2 shows the Kretschmann configuration [3] of the ATR sample consisting of the prism (BK-7) and the LB films on the Al thin films. A He-Ne laser (λ=632.8 nm) and an Ar laser (λ=488.0 nm) were used as the incident lights. The ATR curves, that is, the reflectivities were observed as a function of the incident angle θ at room temperature.

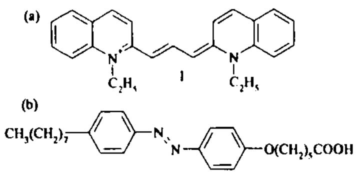

FIGURE 1. The chemical structures of LB molecules: (a) cyanine dye (Cy) and (b) azobenzene (Az).

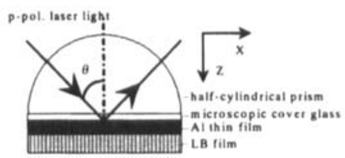

FIGURE 2. The Kretschmann configuration of the ATR sample.

RESULTS AND DISCUSSIONS

Figure 3 shows the ATR properties measured at (a) 632.8 nm and (b) 488.0 nm for the Az LB films adsorbing the Cy dyes before and after annealing. Changes after the annealing were small around the resonant angle of about 45° in the ATR curves at 632.8 nm, but the bottom of the

ATR curve became shallower and wider after the annealing at 100°C. Such a change in the ATR curves corresponded to increase in the imaginary part of the dielectric constants in the z-direction. On the other hand, the bottom around 48° in the ATR curve at 488.0 nm shifted to the lower angle of about 46° after the LB film was annealed at 60 and 100°C. The ATR properties at 488.0 nm showed that the real part of the complex dielectric constants in the z-direction decreased with the annealing.

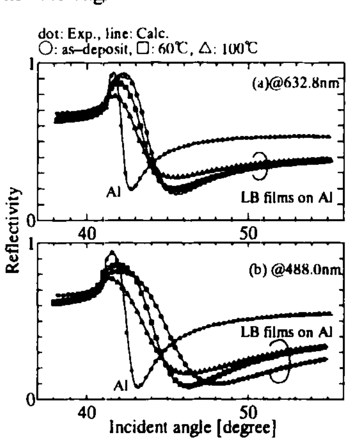

FIGURE 3. ATR curves for the as-deposited and annealed Az LB films measured at (a) 632.8 nm and (b) 488.0 nm.

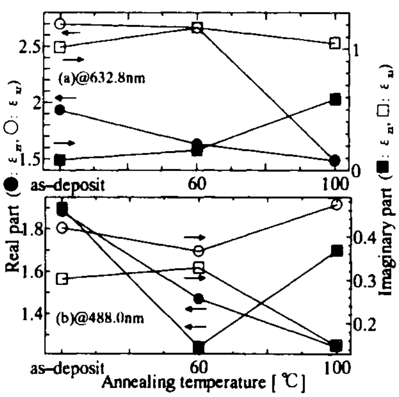

FIGURE 4. Complex dielectric constants of the LB films at (a) 632.8 nm and (b) 488.0 nm calculated from Fig. 3.

Complex dielectric constants of the LB films were calculated from the ATR properties assuming that the thickness of the LB monolayers was 3.6 nm and the LB film was uniaxially anisotropic. Figure 4 shows the complex dielectric constants calculated from Fig.3 using a transfer matrix method[4][5]. In Fig. 4(a), ε_{xi} was almost constant and ε_{zi} increased as the annealing temperature T_A was raised. And the real parts of ε_{zr} and ε_{xr} decreased with the annealing temperature. The subscripts z and x mean the directions shown in Fig.2. And r and i mean the real and the imaginary part of complex dielectric constants. The complex dielectric constants at 488.0 nm changed remarkably as shown in Fig.4(b). Optical absorption properties showed that the orientation of the dyes and the formation of the aggregations varied with the annealing[6][7]. It was thought that the ATR properties and the changes in the complex dielectric constants were caused by the in the dispersion optical absorption depending upon the annealing temperatures.

CONCLUSION

The ATR properties at 632.8 and 488.0 nm were investigated for the Az LB films adsorbing the Cy dyes on Al thin films. The complex dielectric constants were calculated from the ATR curves assuming that the LB films were uniaxially anisotropic. It was thought that the properties were caused by the dispersion properties due to the absorption bands of the LB films. It is very important to evaluate dispersion properties of LB ultrathin films with strong absorption bands for optical applications at various wavelengths.

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