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Evaluation of Photoreactive Azo Dye Molecular Thin Films Utilizing an Optical Interferometer with Evanescent Wave Illumination

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A new Mach-Zehnder type optical-interferometer utilizing evanescent wave illuminations of a reflected beam at a prism surface was constructed to evaluate photoreactive molecular thin films on a prism surface. Refractive index changes of the films due to photoisomerization of azo molecules on the prism caused by an irradiation beam were observed from phase changes between an incident beam and the reflected one at the prism surface. Real-time measurements were also demonstrated using the interferometer microscopy, exhibiting two dimensional distributions of the refractive indices in the molecular films partially excited by the focused irradiation laser beam.

Keywords: azo dye molecular film; evanescent wave interferometer; optical excitation; photoisomerization; refractive index

1. INTRODUCTION

Optical interferometer is one of the useful tools for evaluating the surface profiles, refractive indices and/or thicknesses of the measurement objects [1]. The conventional interferometer has employed an

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optical wave propagating in a free space on the object, which are reflected at the surface and/or passed through the medium causing the phase changes due to the optical interactions. Highly stabilized- and sensitive-measurements can be carried out using a heterodyne phase modulation technique [2,3]. For a practical processing of the optical thin film devices, the combined evaluation system are effective for the *in situ* measurements, such as an atomic force microscope with excitation laser systems in order to observe the optical responses as well as the surface morphologies. However it is very difficult to setup additional equipments above the object surface in the traditional interferometer, because the optical systems occupy these spaces. Furthermore, there are some difficulties for evaluating the multi-layered thin film devices, as long as we use the optical waves in the free space which is never propagating along the boundary of the system. For example, we can not directly access the metallic boundaries of an opaque medium using the propagating waves. This can be resolved by using the evanescent waves of two dimensional surface electromagnetic waves penetrating and propagating along the boundaries via surface plasmon resonance.

A new Mach-Zehnder type optical-interferometer is proposed, in this study, utilizing the evanescent wave illuminations, where the measuring lights are totally reflected at a prism surface. The phases of the reflected light coupled to the evanescent waves are shifted depending on the optical properties of the objects on the prism surface [4]. This optical system allows us to set some other measurement systems on the thin film surface. Some performance can be also carried out during the interferometer measurement. The layer properties of ultrathin film systems can also be evaluated with the help of the localized evanescent waves, because evanescent waves as an optical source of reflected light propagate along the boundaries of the thin film systems [5].

In this study, we demonstrate an observation of photoreactive molecular films utilizing the interferometer of evanescent waves. The optical properties of azo dye molecular thin films were evaluated from the phase measurements of the totally reflected laser beams. Two dimensional distributions of refractive index changes and its optical responses due to the photoisomerization processes were also observed for the azo films partially excited by focused laser beams. For the extensive device-applications of the azo molecular films [6], such as an optically-induced orientation-layer of liquid crystal molecules [7–9], it is very important to evaluate the optical properties of the azo molecular thin films.

2. METHOD AND EXPERIMENTAL SETUP

Figure 1 shows the evanescent wave interferometer system developed in this study and the sample setup to evaluate thin films. The system was constructed as a Mach-Zehnder type interferometer. Rectangular prism (Bk7, refractive index 1.517) was used for generating evanescent waves on the sample substrate. He-Ne laser with wavelength 543 nm was divided into two light beams. The one beam as a measurement light was totally reflected on the prism surface to generate evanescent wave illuminations, and the other was used for a reference beam. The differences of optical length between two optical paths were maintained within the optical coherence length of the used laser. The polarization of the incident light and the incident angle were set to be s-polarization and $\theta = 45$ deg., respectively. The reflected light at the prism surface, interacting with the thin film through the evanescent waves on prism surface, was interfered with the reference beam in order to detect the phase information.

Thin films of azo dye molecules showing photoisomerization were deposited on glass substrates and the samples were set on the prism surface in the measurement. During a part of the films were being irradiated by excitation lasers with 3 mW at various wavelengths: 458, 515 and 632.8 nm, the intensity changes of the interference fringes, that is, the phase shifts were observed at the irradiation area

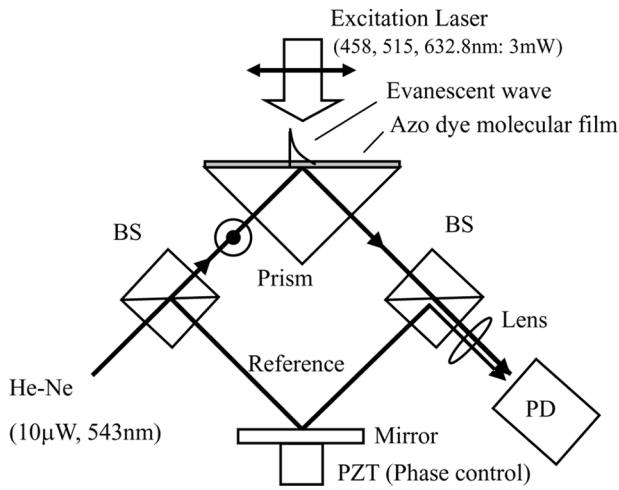

FIGURE 1 Mach-Zehnder type interferometer with evanescent wave illumination developed in this study and sample setup to evaluate photoreactive azo dye molecular films.

using a photo diode (PD). A piezoelectric transducer (PZT) with a mirror was equipped in the optical path of the reference beam in order to control the phase difference between the reflected light and the reference light. The excitation laser can easily be set on the upper space of the prism surface, because our setup has no any optical measuring systems above the sample film. This system provides a great advantage for the *in-situ* measurements of the films. In the example of Figure 1, an excitation laser beam was introduced in the direction normal to the sample surface on the prism for the photoisomerization of the azo dye molecular film.

The phase changes of the reflected beam can be estimated using Fresnel's law with transfer matrix theory for the three layer system of prism/molecular-film/air. The phase of the reflected beam can be calculated by the argument φ of the complex reflection-coefficient, r, given by [4,10]

$$r = |r| \exp(i\varphi) = \frac{r_{12} + r_{23}e^{2ib}}{1 + r_{12}r_{23}e^{2ib}} \tag{1}$$

where φ is the argument, r_{12} and r_{23} are the reflection coefficients at the boundaries of the prism/molecular-film and the film/air, respectively, and the polarization of incident light is s-polarization. The coefficient b of the exponential terms is given by the equation $b = \frac{2\pi}{\lambda} h \sqrt{\hat{n}_2^2 - n_1^2 \sin\theta}$, where λ the wavelength of the incident light in vacuum, h the thickness of the molecular film. n_1 is the refractive indices of the prism, and the $\hat{n}_2$ is the complex one of molecular film given by $\hat{n}_2 = n_2 + i\kappa_2$. The phases approximately linearly increase with the refractive indices of the molecular films on the prism surface.

In this study, Congo Red (CR) azo molecules were used as an example of photoreactive ones [8,9]. The photoisomerization processes have been investigated in the paper of Refs. 11 and 12. The CR molecular films were spin-coated on a microscope cover glass and attached to the prism surface using matching oil. The glass substrate has the same refractive index as the prism. The film thickness was approximately 40 nm when the molecular concentration for the spin-coating was 0.01 mol/L in a water solution. The absorption spectrum is shown in Figure 2. The films can be irradiated by the excitation laser beam coming from the free space on the prism surface. The refractive index of CR molecules is the real part $n_2 = 1.4$ and imaginary part $\kappa_2 = 0.4$ at the wavelength 523 nm [13]. The refractive indices of the azo dye film in the area irradiated by the excitation laser beam are changed, because the molecular concentration of the *trans* state decreases due to the photoisomerization processes between the *trans* state and the

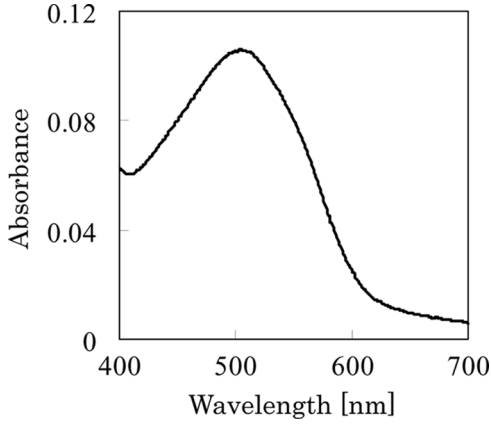

FIGURE 2 Absorption spectrum of Congo Red (CR) molecular thin film.

cis one [6,14]. The ratio $\Delta\varphi/\Delta n_2$ of the phase changes for the refractive indices is estimated to be 0.016 deg. by using Eq. (1).

3. RESULTS AND DISCUSSIONS

Figures 3 (a) and (b) show the absorption spectrum of the CR molecular film and the phase shifts measured by the interferometer utilizing evanescent wave illuminations. The CR films were irradiated, as shown in Figure 1, by three different lasers respectively with the wavelengths 458 and 515 nm around the optical absorption peak, and 632.8 nm of the off resonance. The excitation lasers with the p-polarization have the same intensity 3 mW and the beam diameter 1.5 mm. The intensity of the measurement beam and reference one (He-Ne laser, 543 nm) was set to be 10 μW that were sufficiently weak to prevent the molecular isomerization causing the significant phase changes during the typical measurement time within 1 minute. The phases were calculated from the interference signals sinusoidally varying for the refractive index changes, assuming that each optical beam of the reflected light and the reference light has the same amplitude.

As shown in Figure 3(a), the phase signals increased and saturated by the irradiation of the excitation lasers at 458 nm and 515 nm. But there were no significant changes by the irradiation at 632.8 nm because the molecules are not excited at the wavelength. The phase change $\Delta\varphi$ was 0.12 radians for the irradiations at 458 nm and 515 nm for 10 sec. This phase shift approximately corresponded to

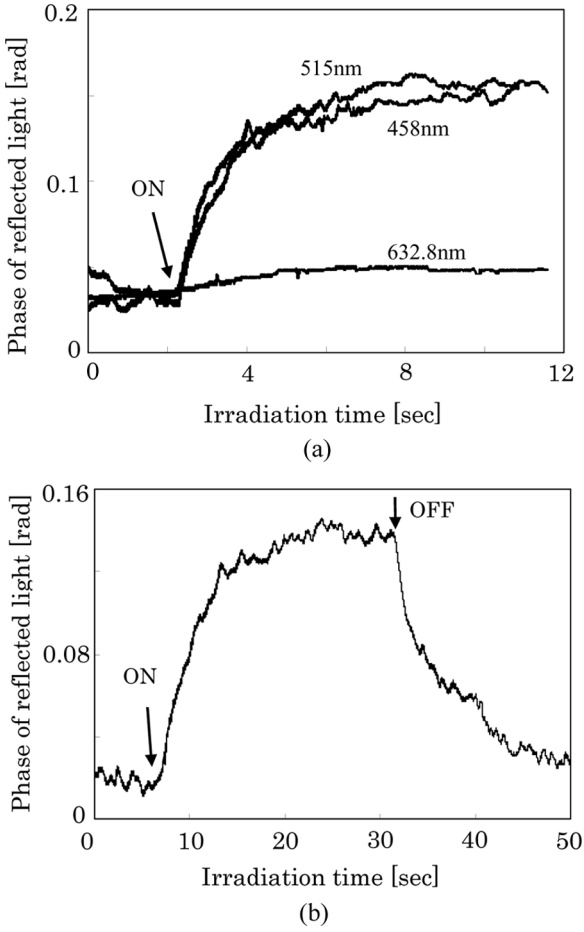

FIGURE 3 Phase changes of reflected light for CR film irradiated by laser beams with wavelengths 458 nm, 515 nm and 632.8 nm (a), and the typical transient property of the phase changes for the CR film irradiated by 515 nm (b).

the changes of the refractive index $\Delta n = 0.04$, assuming that the film thickness was constant before and after the irradiation of the excitation laser beam. It should be noted that the direction of the phase shifts can be determined by the initial phase before the irradiations. The phases differences between the reading and reference beam were controlled by the PZT put in the reference beam of the interferometer, and the initial phases in the experiments were set to shift to the positive direction as the phase of the reading light was decreasing. Figure 3(b)

shows the on/off properties of the phase changes for the irradiation at 515 nm. After switching on the excitation laser, the phase signal increased and saturated with time constant of 3.6 second. After switching off, the phase signal exponentially decreased with that of 4.7 second. The phenomena clearly show that the CR molecules are transformed to be *cis* type and *trans* one due to the isomerization by means of the irradiation and the thermal relaxation without the laser beam, respectively.

Figure 4 shows the phase changes as a function of excitation energy of the excitation laser at the wavelength of 515 nm, where the phase shifts were measured after 30 sec. irradiation with pre-adjusted laser-power that was enough for the signal saturation as shown in Figure 3. The phases increased with the irradiation energy, so that the refractive indices of the CR films decreased with the power of the irradiation. It is tentatively estimated that the irradiation of p-polarized laser increase the number of *trans* type CR molecules mainly oriented in plane of the electric field vector of reading light, and the increase of the in-plane indices depending on the molecular orientations was measured by means of the reflected beam with s-polarized evanescent wave illumination in the interferometer.

The interferometer using evanescent waves was modified to an extended microscope system in order to observe two-dimensional (2D) distribution of the refractive index changes in the CR film as shown in Figure 5. A charge coupled device camera (CCD) with

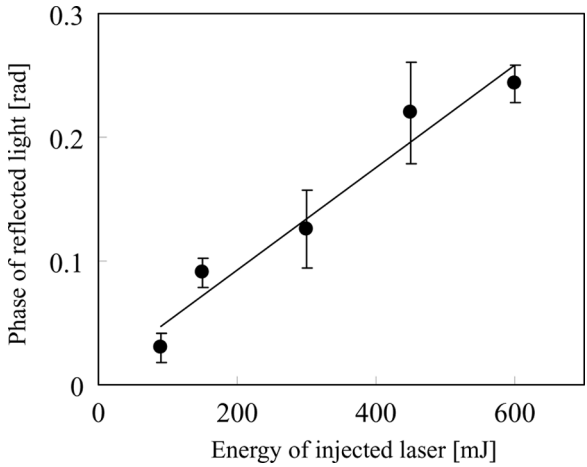

FIGURE 4 Excitation energy dependence of the phase changes for CR molecular thin film.

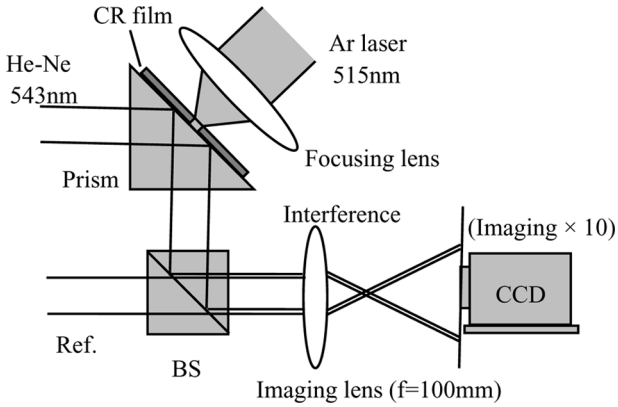

FIGURE 5 Extended microscope system modified from evanescent waves interferometer.

640/480 pixels was used as the optical detector taking the interference images in this system. The images of the CR film were focused on the acceptance surface of the CCD using the objective lens. The magnification ratio was set to be approximately 10 times providing a lateral spatial-resolution about 1 μm for the single pixel of the CCD. The excitation laser beam with 10 mW at the wavelength of 515 nm irradiated a part of the films in the direction of surface normal, using an optical lens with the focusing length 100 mm. The size of the irradiated spot was sufficiently smaller than the total imaging area of the reflected laser beam.

Figures 6(a) shows the typical top-view image for the 500 μm × 370 μm area on the CR film. The phase shift image of CR film due to the refractive index changes after 5 sec. irradiation was observed using the microscope system. The spatial phase changes on the CR film were exactly corresponding to the laser spot size with the diameter of 100 μm. Some radial changes of the small phase shifts were also measured around the laser spot that were cased by scattering light at the boundaries between the film/air and/or glass substrate.

Figure 6(b) shows the transient properties of the phase changes at the different position A, B and C, indicated in the top view of Figure 6(a), during turning on and off the excitation laser beam. These data were measured using the single pixel of the CCD. The position A is close to the center of the irradiation spot where the intensity was approximately maximum in the electric field profile of the irradiation laser with Gaussian distribution. The phase change signals at the

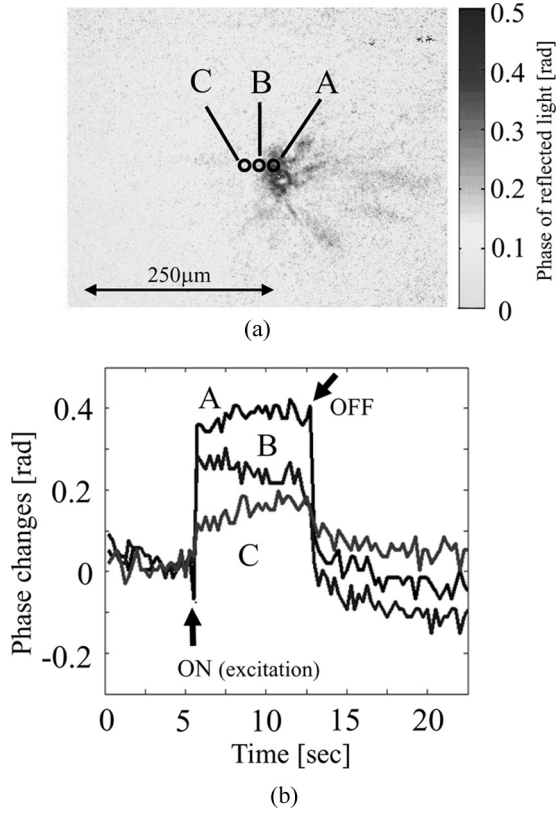

FIGURE 6 Typical top view of the interferometer-microscope image observed for the CR molecular thin film partially excited by focused laser beam (a), and transient properties of the phase changes at the different positions during turning on and off laser irradiation (b).

three points quickly rose after switching on the irradiation, because the power density of the irradiation light was much larger than that in the case of Figure 3. The amount of the phase changes depended upon the position, and the corresponding absolute changes of the refractive indices were estimated to be approximately 0.1, 0.07 and 0.03 at the positions A, B and C, respectively. The decay properties of the signals after turn off also differ for each position. These results clearly show that we have successfully achieved 2D measurements of the optical reactions of the azo molecular thin films simultaneously with the position selectivity and real time measurements using the extended microscope system with CCD.

4. CONCLUSION

The interferometer using the evanescent waves was developed in order to investigate refractive index changes in thin films on a prism. The refractive index changes in the azo dye molecular films irradiated by the laser beams were evaluated from phase changes in the interferometer signals. The spatial distribution of the refractive indices of the film was also observed using the extended interferometer microscopy with CCD. The new evaluation method utilizing low dimensional surface optical waves will be very useful for the applications of sensors for a living biological specimen [15] and various adsorption processes of chemical materials in solutions and harmful gases.

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