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Photooptical Switching of Polymer Film Waveguide Containing Photochromic Diarylethenes

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Fabrication of a photooptical switching device based on the photo-induced refractive index change of polymer film doped with photochromic compounds is described. 1,2-bis(2-methylbenzo[b]thiophen-3-yl) perfluorocyclopentene (BFCP) and 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE) were used as the photochromic compounds. A transformation in the compounds from the opened-ring to closed-ring form was induced by irradiation with a He-Cd laser (325 nm) and the reverse reaction with an Ar ion laser (488 nm). The polymer films containing BFCP and CMTE showed a refractive index change, Δn, as large as 5×10^{-4}/wt% photoisomerized chromophores. Photooptical switching of a prism-coupling device was demonstrated by alternate irradiation with Ar ion and He-Cd lasers, and also by irradiation with a pulsed YAG laser.

KEYWORDS: photochromic compound, diarylethene, polymer film, switching device, waveguide, prism coupling, refractive index

1. Introduction

Much attention has been paid to developing optical devices capable of signal processing such as switching, deflection, and modulation. Almost all devices proposed to date are based upon electro-, acousto-, or magnetooptical effects. The device that can control light directly by using a photooptical effect[1,2] (*e.g.*, photo-induced refractive index change) is of interest,[3] since it can operate without mechanical motion and electric noise. In this study, fabrication of a photooptical switching device based on the photo-induced refractive index change of polymer film containing photochromic compounds is described.

A photochromic compound is characterized by its ability to undergo a reversible transformation between two different chemical forms having different absorption spectra in response to light of appropriate wavelengths.

$$A \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} B$$

Recently, a new type of photochromic compounds, diarylethenes, which undergo thermally irreversible and fatigue-resistant photochromic reactions, was developed.[4,5] Both isomers were found to be stable for more than 3 months at 80°C, and coloration/decoloration cycles of the compounds can be repeated more than 10^4 times. In this study, such diarylethene-type photochromic compounds were dispersed in polymer film and used for photooptical switching devices.

2. Experimental

2.1 *Materials and sample preparation*

1, 2 - bis (2-methylbenzo [b] thiophen - 3 - yl) perfluorocyclopentene (BFCP) and 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE) were used as the photochromic compounds. A transformation in the compounds from the open-ring to closed-ring form was induced by irradiation with He–Cd laser light (325 nm) and the reverse reaction with Ar ion laser light (488 nm) as shown in Fig. 1. The compounds were dispersed in amorphous polyolefin (Zeonex 280) and used for the waveguide.

The polyolefin film waveguide was prepared by spin-coating a toluene solution containing the polyolefin and the photochromic compounds (20 wt%) on a Pyrex substrate (index of refraction, $n_s=1.47$). The polymer film was kept at 70°C for 24 h under vacuum to remove the solvent. The film thickness was about 4 μm.

2.2 *Prism-coupling method for refractive index measurement*

Determination of the refractive index of the waveguide was carried out using the prism-coupling method. This method is convenient and accurate and well described in the literature.[6,7] The experimental setup for the prism-coupling method is illustrated in Fig. 2. Here two prism input-output couplers were used. The TE-polarized He-Ne laser beam (wavelength 633 nm) was focused on the edge of the prism coupler (index of refraction, $n_p=1.78$), which was brought into contact with the film. The He–Ne laser beam was transferred to a guided wave by the prism at appropriate coupling angles. The effective mode index n_{eff} was calculated for each mode from the angles at which light was coupled to the guides using the relation[8]

$$n_{eff}=n_p \sin\left[\alpha+\sin^{-1}\frac{(\sin\theta)}{n_p}\right], \quad (1)$$

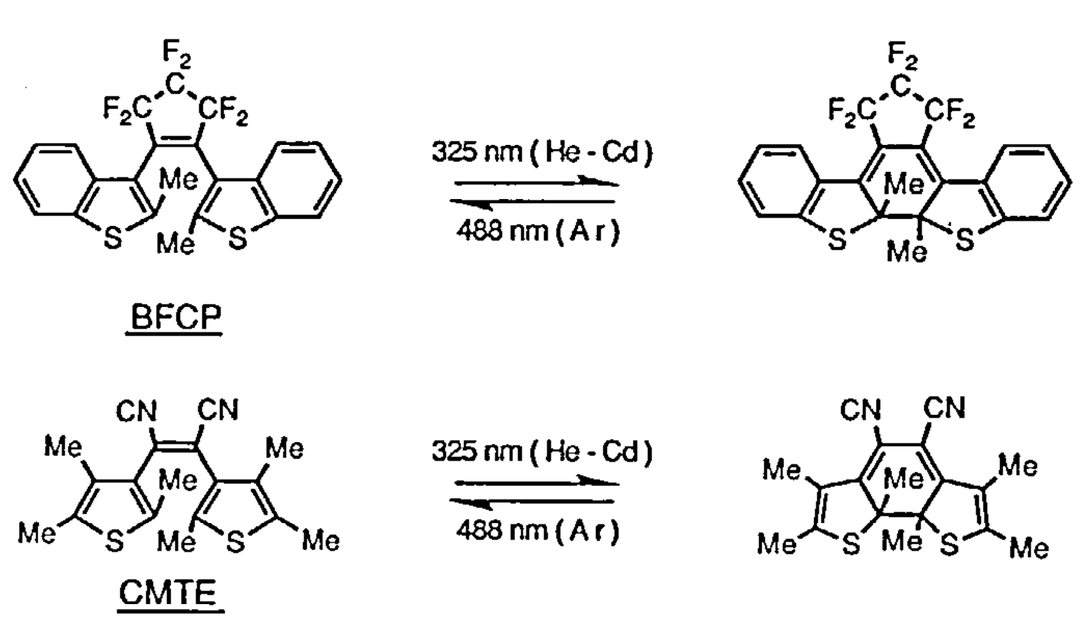

Fig. 1. Photochromic compounds.

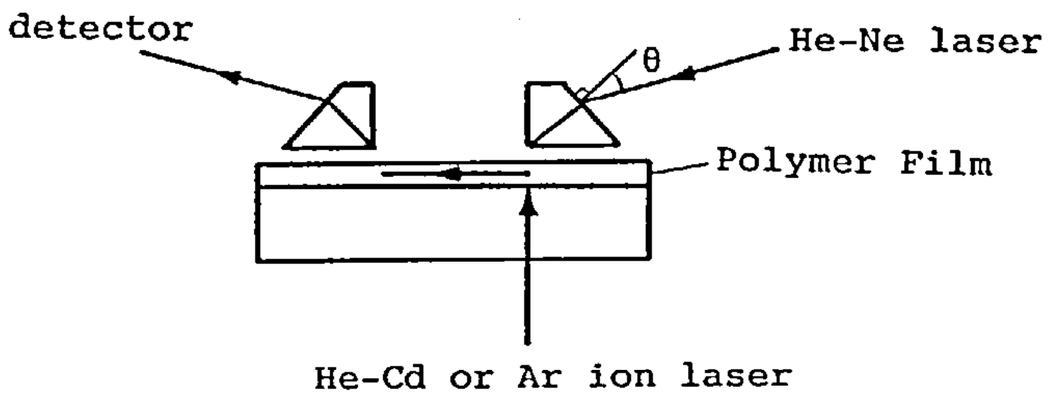

Fig. 2. Illustration of the prism-coupling method.

where n_p and α are the prism refractive index and angle, respectively, and θ is the coupling angle from the prism normal. The dispersion mode of the polymer film waveguide was calculated from the coupling angles, and the refractive indices were determined.[6]

3. Results and Discussion

The absorption spectral change of the polyolefin waveguide film containing BFCP (20 wt%) is shown in Fig. 3. Irradiation of the film with He–Cd laser light led to the formation of a red film in which visible absorption at 520 nm was observed. Upon Ar ion laser light irradiation, the red color disappeared. Figure 4 shows the coupling characteristics of the TE_0-mode, i.e., output light intensity as a function of the incident angle, for the waveguide by irradiation with Ar ion and He–Cd laser light. The coupling characteristics shifted to a higher angle, and the refractive index increased when the film was irradiated with a He–Cd laser (in the case of Fig. 4, the photo-induced refractive index change is about 1.5×10^{-3}). Upon irradiation with an Ar ion laser, the coupling angle returned to the initial state. The angle shifts correlated well with the amount of isomerization of BFCP.

Figure 5 shows the relationship between the weight fraction of the photoisomerized compounds in the film and the refractive index change (Δn). BFCP of 10 wt% undergoes photoisomerization in polymer matrices under suitable conditions. In this case, the photo-induced refractive index change reaches 5×10^{-3}. Figure 6 shows the result for the waveguide film containing CMTE. The photo-induced refractive index change observed for CMTE film was as large as the change for the BFCP film.

Refractive index (n_d) of the compounds can be esti-

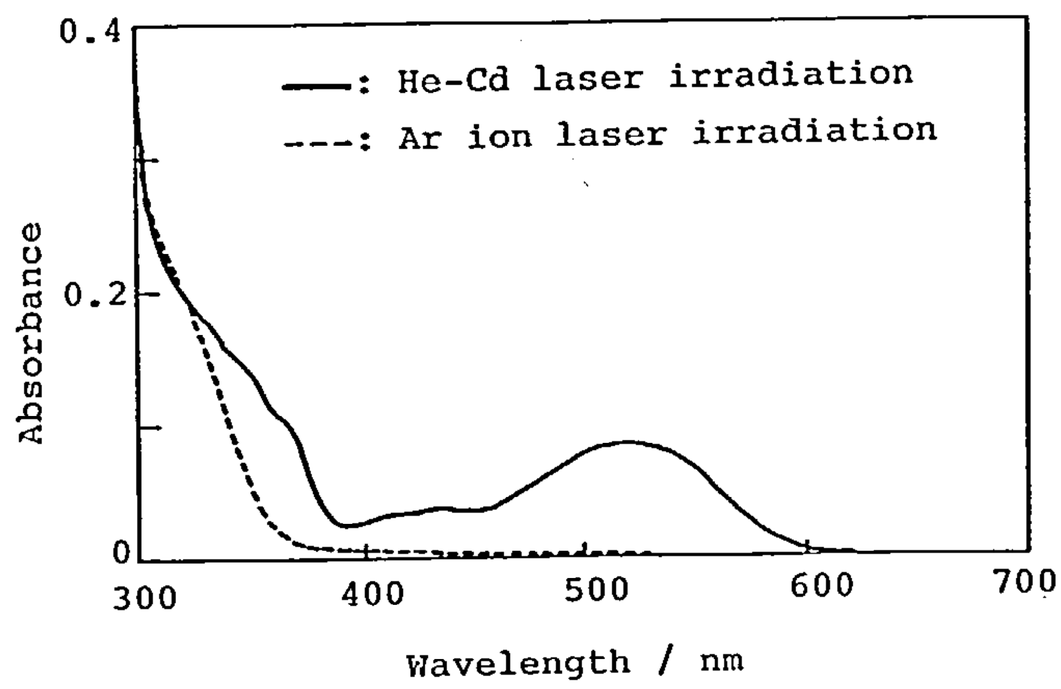

Fig. 3. Absorption spectral change of polyolefin film doped with BFCP.

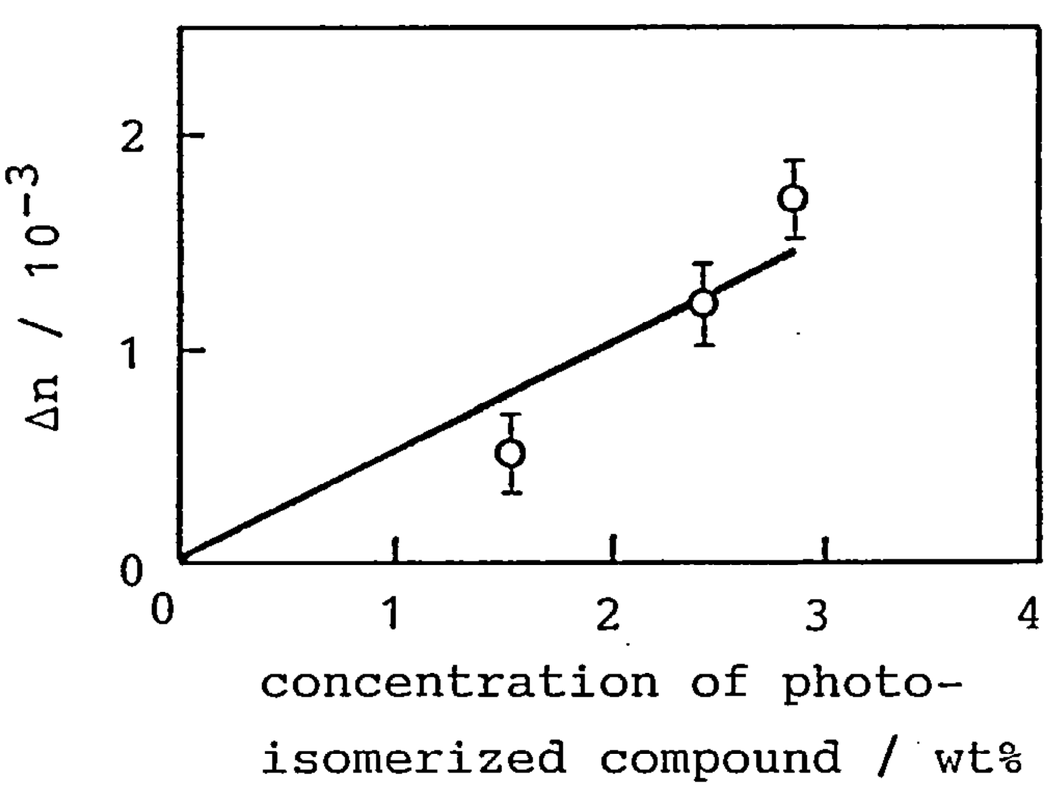

Fig. 5. Photo-induced refractive index change (Δn) for BFCP.

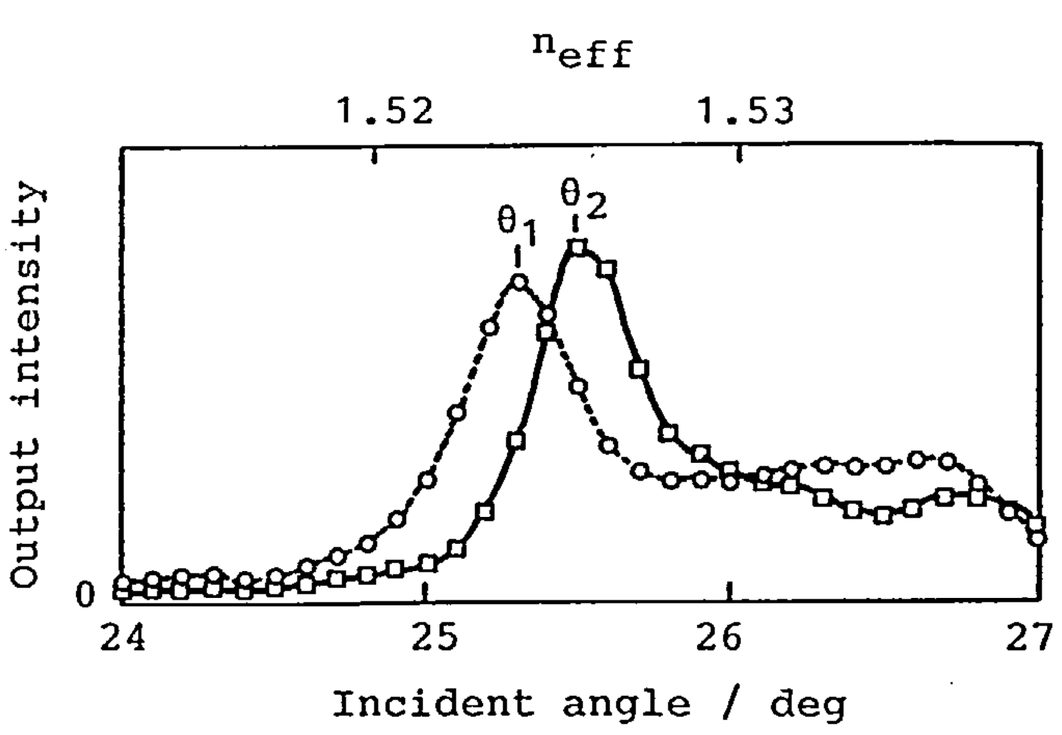

Fig. 4. Coupling characteristics of BFCP-doped polyolefin waveguide. ○: under irradiation with Ar ion laser light □: under irradiation with He-Cd laser light

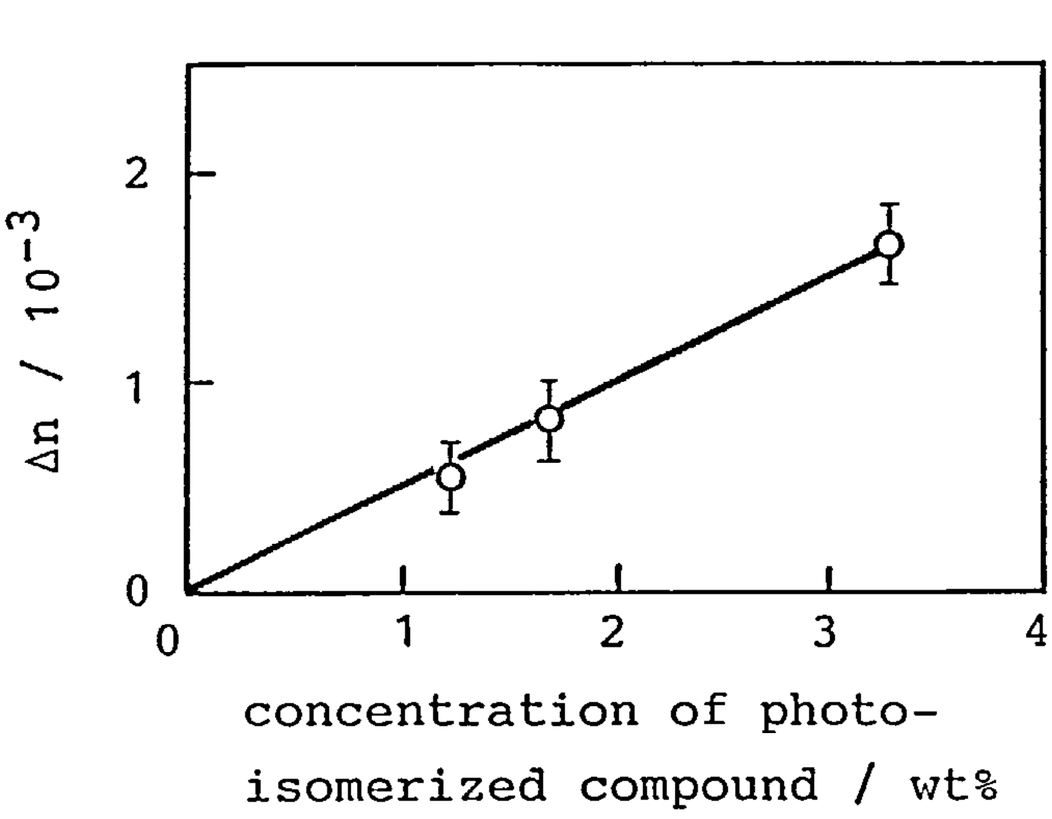

Fig. 6. Photo-induced refractive index change (Δn) for CMTE.

mated from molecular refraction ($[R]$) and molecular volume (V).

$$n_d = \sqrt{(2\phi+1)/(1-\phi)}$$
$$\phi \equiv [R]/V \quad (2)$$

Using eq. (2), the photo-induced refractive index changes of BFCP and CMTE with 10 wt% photoisomerization was calculated to be 5×10^{-4}. The observed value was 10 times larger than the calculated value. The discrepancy is ascribable to the dispersion effect.

Refractive index varies as a function of wavelength. In the wavelength region far from the absorption bands, the refractive index increases monotonically with decreasing wavelengh. On the other hand, near the absorption band, the refractive index becomes large.[9] The calculated refractive index change, 5×10^{-4}, is the value at the wavelength region far from the absorption bands. This explains the large refractive index change observed at 633 nm in comparison with the calculated value.

The coupling chracteristics shifted to a highter angle by He–Cd laser (325 nm) irradiation, as shown in Fig. 4. Thus, if we set the incident angle at θ_1 or θ_2 of Fig. 4, the output intensity is expected to change by irradiation with Ar ion (488 nm) or He–Cd laser light (325 nm). The switching characteristics of output intensity were investigated under alternate irradiation with 488 nm and 325 nm light. Figure 7 shows the result. At θ_1 (which is the coupling angle under irradiation with Ar

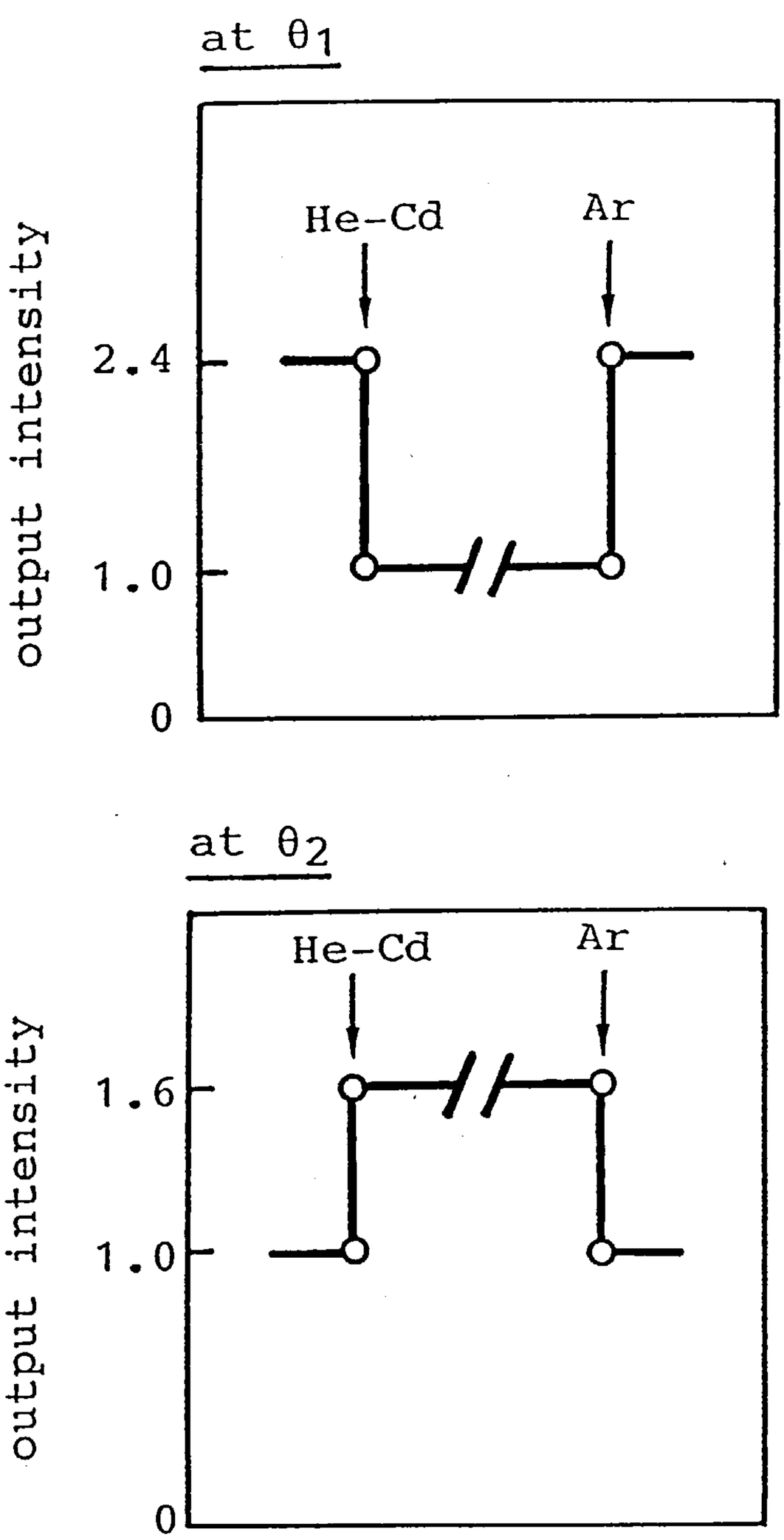

Fig. 7. Change of output intensity for BFCP-doped polyolefin film waveguide.

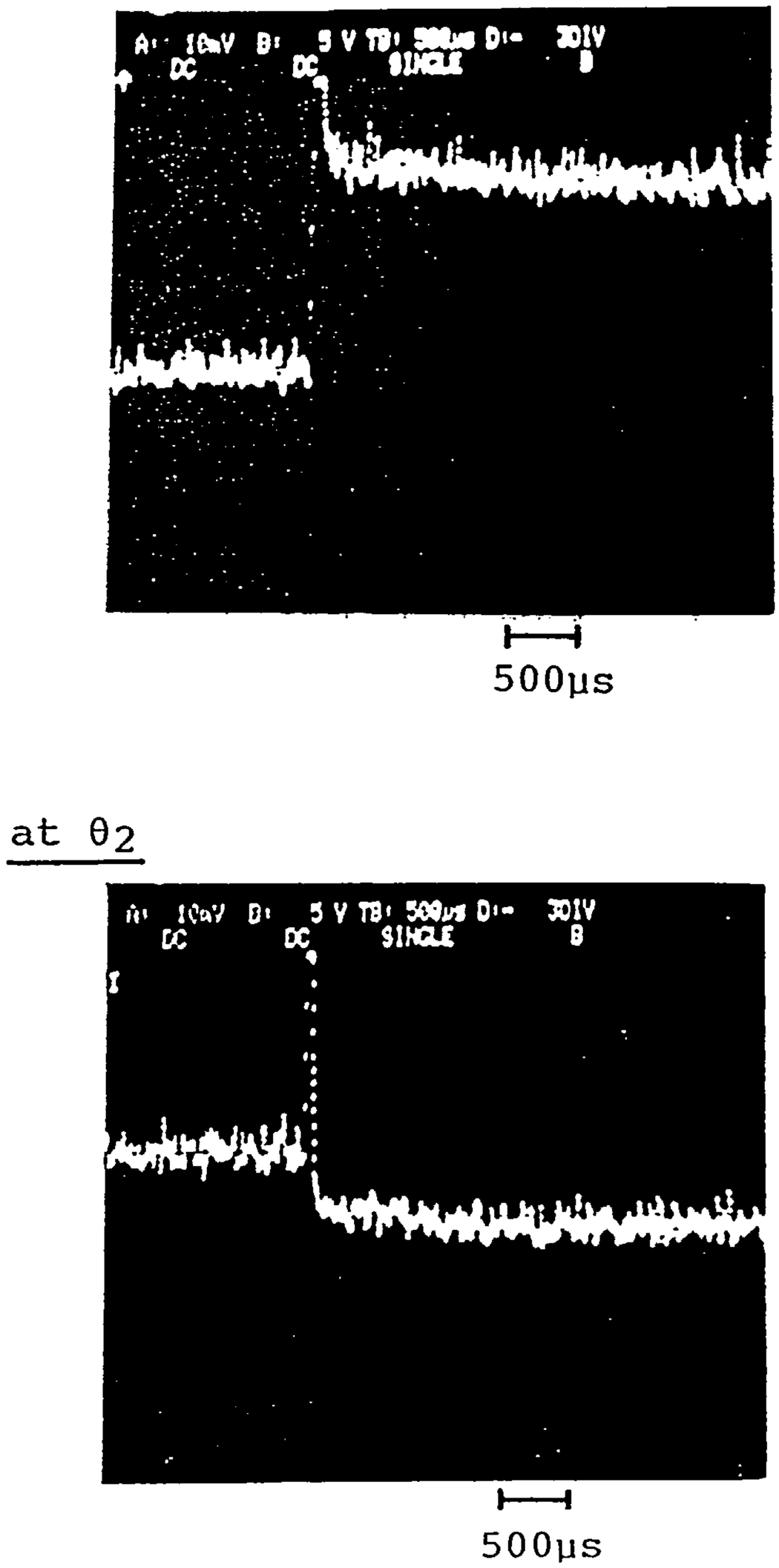

Fig. 8. Change of output intensity for BFCP-doped polyolefin film waveguide by irradiation with a pulsed laser.

ion laser light in Fig. 4), the output intensity decreased upon irradiation with 325 nm light, and recovered upon irradiation with 488 nm light. On the other hand, at θ_2 (which is the coupling angle under irradiation with He–Cd laser light in Fig. 4), the output intensity increased upon irradiation with 325 nm light, and recovered upon irradiation of 488 nm light.

The photoisomerization rates of 2,3-di(2,4,5-trimethyl-3-thienyl)maleic anhydride were studied by a laser photolysis method and both the ring-opening and the ring-closing reactions were found to proceed in less than 100 ps.[10] The rapid response suggests that the switching rate reaches more than 1 GHz. In order to confirm the rapid response rate, the switching characteristics were studied under irradiation with a pulsed laser (pulse width: 8 ns, wavelength: 532 nm, power: 15 mJ), as shown in Fig. 8. At θ_1, the output intensity increased, while at θ_2 the intensity decreased. The response time was less than 100 μs. At present, we could not eliminate the initial spike noise possibly caused by the scattering light. The response time is expected to be shortened to less than 1 ns when the noise is eliminated. The observed rate less than 100 μs is, however, still much faster than the rate observed for chalcogenide films.[2]

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