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# Refractive index change in photochromic diarylethene derivatives and its application to optical switching devices

Mitsutoshi Hoshino *, Fumihiro Ebisawa, Takashi Yoshida, Ken Sukegawa

*NTT Opto-electronics Laboratories, Tokai-mura, Naka-gun, Ibaraki-ken, 319-11, Japan*

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## Abstract

The refractive index change of photochromic diarylethene derivatives in solid polymer was studied with a view to fabricating an optical switching device. The reaction time required for a symmetric diarylethene photochromic compound in a copolymer of fluoroethyl methacrylate and methyl methacrylate (film thickness: 10 μm) was 20–30 s when exposed to UV light (intensity: 5.3 mW $cm^{-2}$ at 350 nm) to form a closed ring and about 10 s with visible light (intensity: 3.7 mW $cm^{-2}$ at 500 nm) to form an open ring. The refractive index change at 1.30 μm, measured with a prism coupler, was 0.0005 per 10 wt.% of diarylethene photochromic compound. The iteration number of the photochromic reactions in the polymer film decreased in the following order: symmetric, asymmetric diarylethene and acid anhydride.

We propose a new type of self-holding optical switch combining a heat stable photochromic material with silica planar lightwave circuits.
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*Keywords*: Refractive index change; Photochromic; Diarylethene derivatives; Optical switching device

## 1. Introduction

We studied both the materials, which are photochromic compounds and their binder polymer, and the fabrication process for making optical switches and were able to develop a good new type of switch.

We investigated some of the properties of photochromic compounds, i.e. the refractive index changes, the photoreaction speed, and the durability of the iteration number of the photoreactions of diarylethene photochromic compounds in order to select an appropriate one. We also designed a process for fabricating a new type of optical switch using this photochromic compound. The micro-optical switch is one of the key devices for constructing an optical communication system [1]. It has to be inexpensive, and highly reliable as regards fabrication and operation and also maintenance free.

It is well known that diarylethenes are capable of reversible photoreactions [2,3]: that is, ring-formation and ring-cleavage photoreactions. They also exhibit heat stable photochromism.

Irie et al. reported a guiding principle for the molecular design of a heat stable diarylethene photochromic compound [4] when they revealed that heat stable diarylethene with heterocyclic rings could be designed based on calculated-state correlation diagrams. That is the introduction of heterocyclic groups with less resonance energy at both terminals of the ethene group makes the resulting compound more heat stable. Many kinds of photochromic compound have been synthesized based on this principle and some of them exhibited heat stability. We selected three of these diarylethene compounds as candidates for use in manufacturing a new type of optical switch. In addition, we have recently synthesized a new type of diarylethene photochromic compound, ourselves [5]. This photochromic compound has a long alkyl chain, and high solubility in binder polymer.

## 2. Experimental

Fig. 1 shows the three photochromic compounds we used in our experiments. Two were fluorinated diarylethene compounds: 1,2-bis(2-methylbenzo[b]thiophen-3-yl) perfluorocyclopentene (DA1) and 1-(2-methyl-3-benzothienyl)-2-(1′,2′-dimethyl-3′-indolyl) perfluorocyclopentene (DA2) (Kobe Tennenbutsu Kagaku Co. Ltd.). The third was 3,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (BTTM) (Tokyo Kasei Co. Ltd.). These three photochromic compounds were used without further purification.

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* Corresponding author. Tel: +81 292 87 7587; fax: +81 292 87 7789; e-mail: hoshino@iba.iecl.ntt.jp

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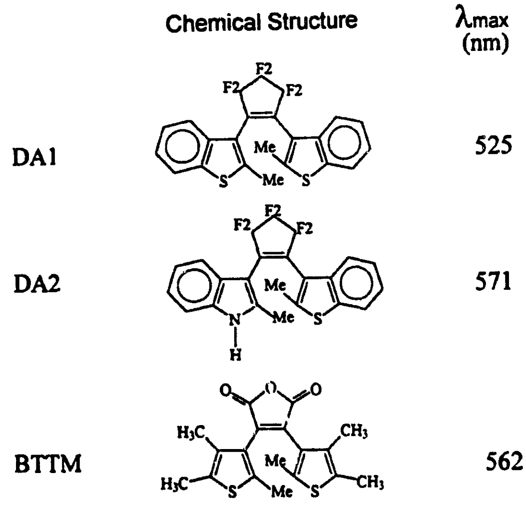


Fig. 1. Chemical structures of three photochromic compounds.

UV light was obtained by filtering the light from a Xe lamp (Ushio Electric Co. Ltd.; power: 1 kW) with a UV-D36C glass filter (Toshiba Glass Co. Ltd.). Visible light was obtained using a Y-50 glass filter (Toshiba Glass Co. Ltd.). The intensity of the UV light was 5.3 mV cm$^{-2}$ (peak wavelength: 350 nm) and that of the visible light was 3.7 mW cm$^{-2}$ at 500 nm.

Polymer films were formed by spin coating a polymer solution. The concentration of the photochromic compounds was 10 wt.% in a copolymer of fluoroethyl methacrylate and methyl methacrylate. The copolymer had a monomer ratio of MMA:FEMA = 16:84. MMA indicates methyl methacrylate and FEMA indicates 2,2,2-trifluoroethyl methacrylate. The name of this copolymer is abbreviated to PFEMA. The polymer solution containing one of the photochromic compounds was soluble in methyl isobutyl ketone (MIBK). The refractive index of the polymer film was measured with a commercially available prism coupler (Metricon Co. Ltd., Model PC-2010) at three wavelengths (0.63, 1.30 and either 1.15 or 1.55 μm). Fig. 2 shows an outline of the prism coupler. When we vary the incident angle of a laser beam to a prism by rotating the prism with a stepping motor, incident laser beams at certain angles are coupled into a mode of the polymer film through the prism and then enter the film and propagate through it. At other incident angles, the laser beam is totally reflected at the bottom of the prism. The intensity of the reflected beam is measured by a photodetector. In the propagating mode ($m = 0, 1, 2, 3, \ldots$) at a discrete beam angle, the wave of the laser beam propagates in the polymer film. At each propagating mode angle, the ratio of the reflected light intensity to the incident light intensity becomes much smaller than the usual total reflected light intensity. The refractive index $n$ of the film and the film thickness $T$ were calculated by using Eqs. (1) and (2) with more than three modes. $n$ is obtained as the value of the convergence of the computational iteration.

$$n^2 = (N_0^2\Phi_2^2 - \Phi_0^2)/(\Phi_2^2 - \Phi_0^2) \tag{1}$$

$$kW(n^2 - N_m^2)^{1/2} = \Psi_m(n, N_m) \tag{2}$$

where $m$ is the mode number. For Eq. (1), $N_m$ is the effective refractive index at mode $m$. The suffixes 0 and 2 for $N$ in Eq. (1) indicate the number of zero and second propagating modes. $\Phi_0$ and $\Phi_2$ are Goos–Hänchen shifts on the film–substrate interfaces and film–air interfaces, respectively. In Eq. (2),

$$\Psi_m(n, N_m) = m\pi + \Phi_0 + \Phi_2 \tag{3}$$

and

$$\Phi_j \equiv \arctan\left[\left(\frac{n}{n_j}\right)^2 \frac{N_m^2 - n_j^2}{n^2 - N_m^2}\right]^{1/2} \tag{4}$$

where the suffix $j$ is 0 or 2 and $n_0$ is the refractive index of the substrate and $n_2$ is the refractive index of the air.

If the calculation is used for three or more modes, the average value and standard deviation of both of refractive index and film thickness can be obtained by the same numerical calculation. The refractive index is calculated to the minus fourth power by the calculation method. The main difference between the prism coupler method and the standard Abbé refractometer is that the former uses the coupled propagating mode of a laser beam in a film specimen.

The refractive index of a bulk substance is calculated in a way similar to the Abbé refractometer method. The refractive index is calculated by using a total reflection equation: that is, $n = n_p \sin\theta$ where $n$ is the refractive index of the bulk substance, $n_p$ is the refractive index of the prism and $\theta$ is the angle of total reflection. Tien et al. described the theory, preparation and evaluation of a prism coupler [6].

The process for preparing the polymer cladding used in this optical switch is as follows: the polymer solution was drawn into a syringe equipped with a tube made of polytetrafluoroethylene with a nozzle. After connecting the syringe containing the polymer solution to an infusion pump (Har-

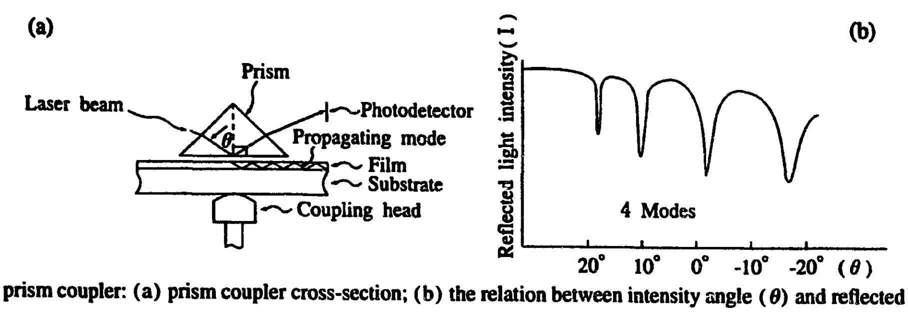


Fig. 2. Outline of prism coupler: (a) prism coupler cross-section; (b) the relation between intensity angle ($\theta$) and reflected light intensity ($I$).

vard Apparatus Co. Ltd., Model 11), we operated the pump to obtain a very slow extrusion rate of about 30–50 ml $h^{-1}$. The polymer solution (polymer concentration: 30–40 wt.%) was extruded onto the silica core of a planar lightwave circuit (PLC) which was moving at a constant speed away from the syringe on an *X–Y* stage. After the extrusion, the MIBK solvent was evaporated from the polymer solution and then a polymer cladding was formed on the silica core. This cladding was 16 mm high, 0.3 mm wide and 45 mm long. Then cladding was heated at 70 °C for 10 h in an air oven in order to increase its adhesion to the silica core. The method for preparing our new switch has been reported elsewhere [7].

## 3. Results and discussion

Figs. 3–5 show the visible spectrum changes of DA1, DA2 and BTTM according to the time of UV irradiation after a previous visible light exposure. The maximum absorbance wavelength of these three photochromic compounds was 515 nm for DA1, 571 nm for DA2 and 560 nm for BTTM.

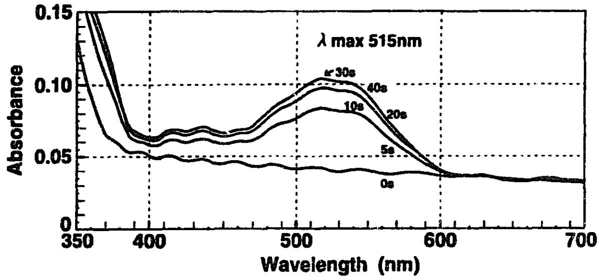


Fig. 3. Dependence of change in visible spectrum of DA1 on UV irradiation time.

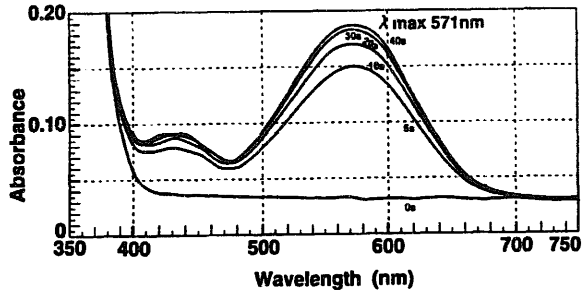


Fig. 4. Dependence of change in visible spectrum of DA2 on UV irradiation time.

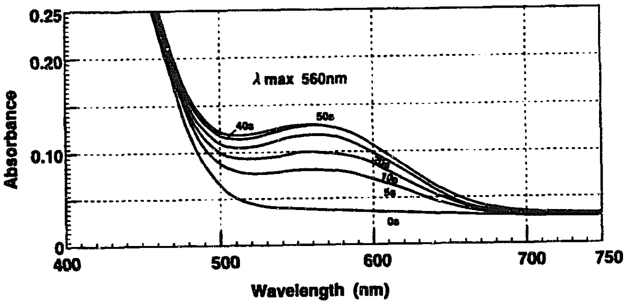
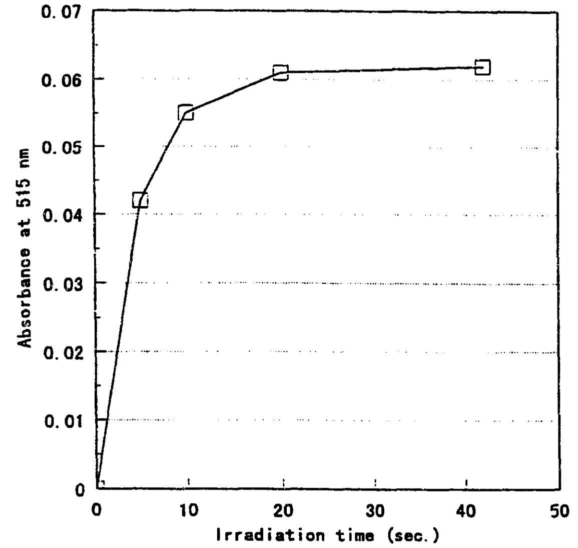
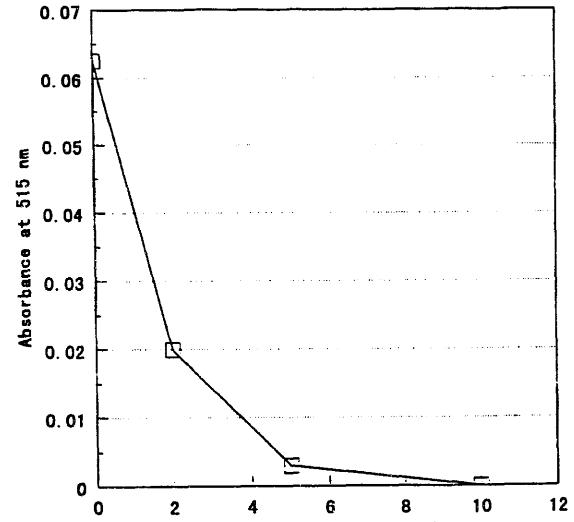


Fig. 5. Dependence of change in visible spectrum of BTTM on UV irradiation time.



Filter for UV light : UV-D36C
Light source : Xe lamp
Photochromic compound : DA1

Fig. 6. Relation between the absorbance of DA1 at 515 nm ($\lambda_{max}$) and UV irradiation time.



Filter for visible light : Y-50
Light source : Xe lamp
Photochromic compound : DA1

Fig. 7. Relation between the absorbance of DA1 at 515 nm ($\lambda_{max}$) and visible light irradiation time.

Figs. 6 and 7 show the respective relations between the absorbances of DA1 at 515 nm ($l_{max}$) and the UV and visible light irradiation times. The coloration reaction in solid polymer (PFEMA) film (10 μm thick) took about 20–30 s under UV irradiation and the discoloration reaction took about 10 s under visible light irradiation. The photochromic reaction of one molecule seems to require about 10 ps [8] but the reaction time of photochromic compounds in the polymer film was much longer. This is because molecular motion is easy in solution. So the photochromism proceeds very quickly. By contrast, the molecules of photochromic substances are immobilized, that is, surrounded by solid polymer or hard

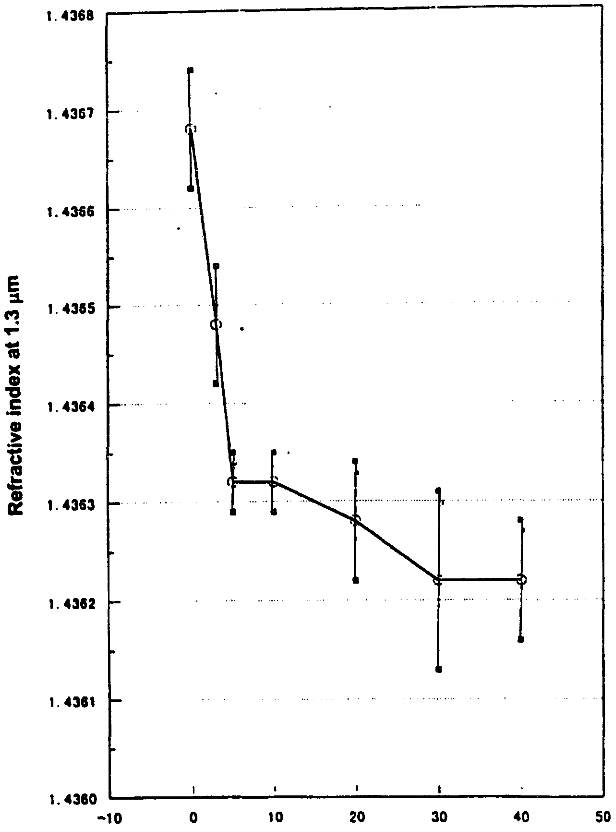


Fig. 8. Refractive index change in DA1 caused by the irradiation of visible light with a peak of 533 nm.

gel. This state causes molecular dynamics to be slowed significantly. Furthermore as photochromic compounds also have large UV and visible light absorbance, the intensity of the irradiated UV and visible lights in a polymer film decay exponentially according to the polymer depth depending on the absorbance of the photochromic compound being used. For the above two reasons, the reaction time of photochromism in polymer film will be prolonged. One effective method for shortening the switching time of this device, is to employ photochromic compounds that are in a mobile state such as solutions or soft gels.

Fig. 8 shows the refractive index change in DA1 caused by the irradiation of visible light with a peak of 533 nm. The refractive index decrease was measured by attaching the polymer film to a prism coupler under visible light irradiation with a He–Ne laser at constant temperature and humidity. As shown in Fig. 7, the absorbances of the film containing DA1 decreased drastically during the first 5 min of visible light irradiation. This irradiation caused a rapid decrease in the refractive index during this period. This shows that the intensity of the irradiated visible light in the polymer film was proportional to the absorbance of visible light in DA1 which causes a change in the conformation of the photochromic molecules from a closed-ring to an open-ring isomer. The total refractive index change at 1.30 μm and 20 °C was 0.0005 per 10 wt.% diarylethene photochromic compound in PFEMA. The refractive index change was of the minus fourth power in the polymer film containing 10 wt.% of DA1. As described later, a change value of 0.0005 was sufficient for full light switching. If the refractive index change were double the initial value, this optical switch can be shortened to half its initial length. The degree of refractive index change is controlled exactly by the UV light irradiation time. The switching state of a light circuit can be maintained without using any external power source.

Table 1
Refractive index changes of PFEMA films containing 10 wt.% of photochromic compound and the absorbances of the three compounds

| Name | Refractive index change [a] | Absorbance [b] |
|---|---|---|
| DA1 | 0.0005 | 0.11 |
| DA2 | 0.0012 | 0.18 |
| BTTM | 0.0004 | 0.065 |

[a] Wavelength: 1.3 μm; photochromic concentration: 10 wt.%.
[b] Film thickness: 10 μm.

The refractive index change of DA2 was about twice that of DA1, but it was difficult to measure the change precisely. The refractive index was easily affected by the surrounding atmosphere, that is, humidity, temperature, and the location of the specimen sample. The absorbance of DA2 was also about twice that of DA1. The order of the refractive index change may agree with the order of the absorbance change of the photochromism. The refractive index change was estimated to be synchronous with the photochromic reaction.

Table 1 shows the refractive index changes of PFEMA films containing 10 wt.% photochromic compound and the absorbances of the three compounds. These results show that the order of refractive index change is in agreement with the order of absorbances. The refractive index change of DA2 was about twice that of DA1, as was the absorbance. This may indicate that the order of the refractive index change agrees with the order of the absorbance change of the photochromism. These compounds exhibit refractive index changes with 10 wt.% polymer of a minus fourth order, nevertheless this is sufficient for our use.

Fig. 9 shows the relation between the absorbances of the three photochromic compounds and iteration numbers of alternate UV and visible light irradiation. BTTM had the least stability in terms of iteration, in that the absorbance decreased in around ten cycles of irradiation. The stability of DA2 was between those of the other two compounds, and its absorbance decreased in about 30 cycles of irradiation. DA1 was the most stable. Its absorbance held at its initial value for up to 200 iterations. Moreover, its absorbance decrease was slower than that of the other two compounds.

Figs. 10–12 show the visible spectrum changes of the three photochromic compounds with alternative UV and visible light irradiations at each iteration number. No new absorption occurred in the visible spectra during the visible light irradiation of the polymer films containing a photochromic compound. This result shows that no side reaction occurs during

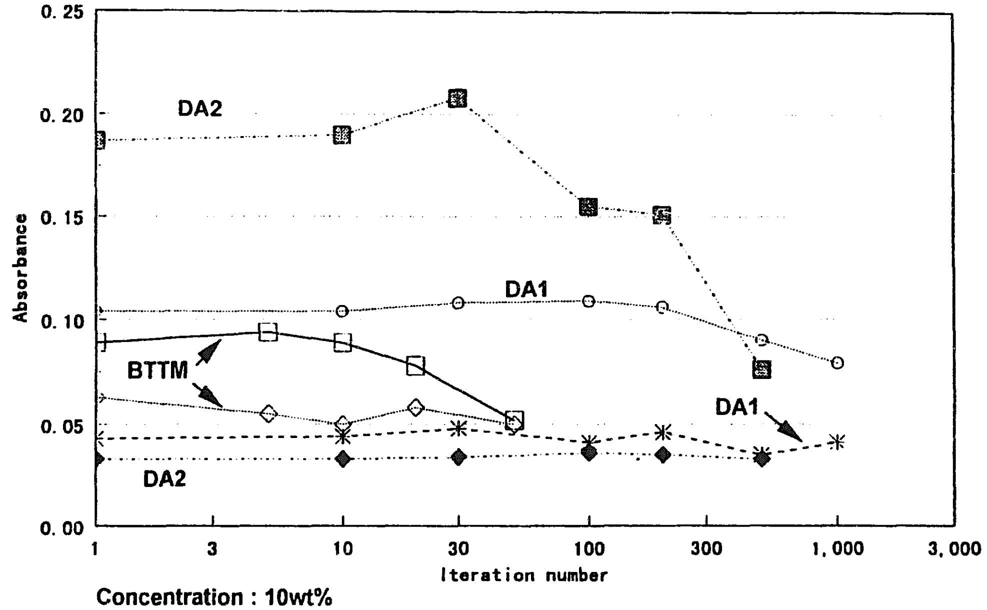


Fig. 9. Relation between the absorbances of the three photochromic compounds and iteration numbers of alternate UV and visible light irradiation.

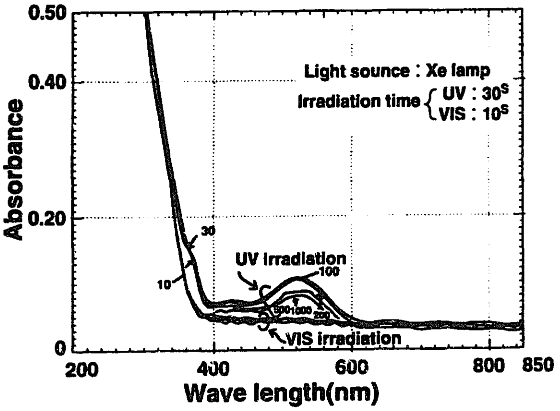


Fig. 10. Visible spectrum changes of DA1 with alternating UV and visible light irradiations at each iteration number.

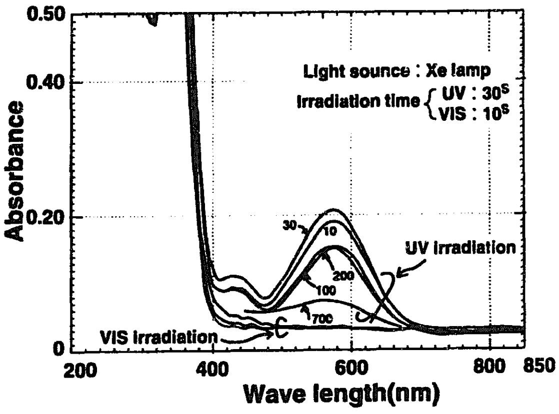


Fig. 11. Visible spectrum changes of DA2 with alternating UV and visible light irradiations at each iteration number.

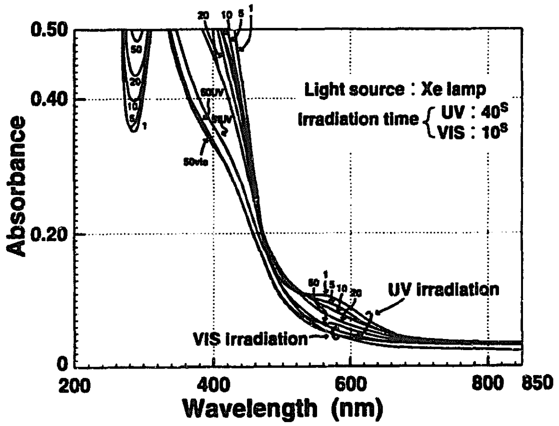


Fig. 12. Visible spectrum changes of BTTM with alternating UV and visible light irradiations at each iteration number.

the reaction which causes the open-ring isomer formation of the photochromic compound. However, because considerable decreases were observed in the absorbances after given UV irradiation times, the iteration durability of the diarylethene photochromic compounds were ruled mainly by the reaction scheme of the closed-ring isomer formation. It is estimated that there was some photodegradation in which intermediates reacted with oxygen radicals during the formation of the closed-ring isomer [9].

The iteration resistivities of the three photochromic compounds in the polymer films decreased in the following order: symmetric (DA1), asymmetric diarylethene (DA2) and acid anhydride (BTTM). The fact that BTTM had the lowest resistivity was thought to be because of the high elimination tendency of the methyl group attached to the thienyl rings.

The results for all three photochromic compounds show a small increase in the equilibrium absorbance just before it decreases steeply. The equilibrium absorbances which were the optical densities of the photochromic compounds immediately after UV irradiation, gradually increased along with the UV irradiation number. These phenomena may be caused by the increase in the free volume of the photochromic compounds in solid polymers.

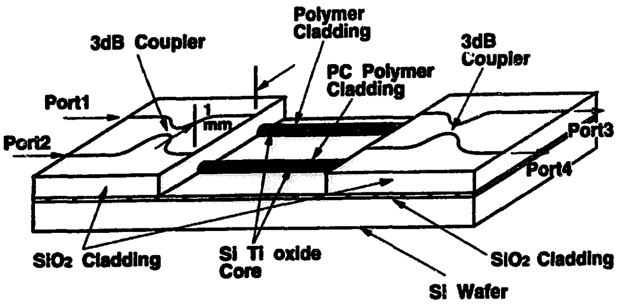


Fig. 13. Schematic view of proposed optical switch.

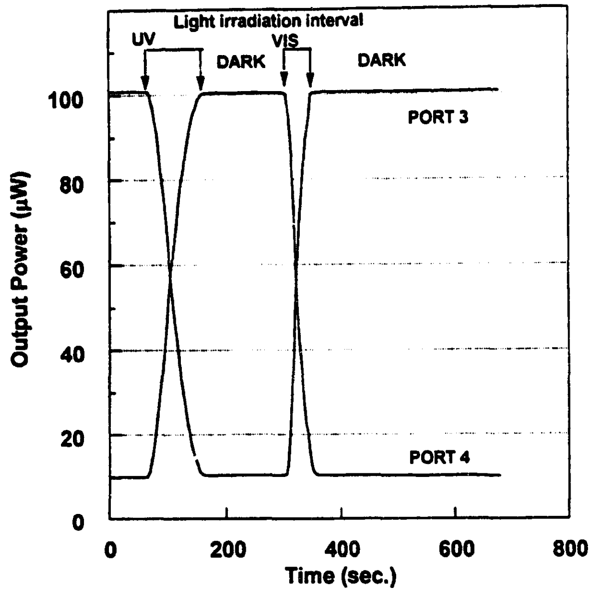


Fig. 14. Relation between output power and irradiation time of proposed switch with alternating UV and visible light irradiation.

We have proposed a new optical communication device combining these organic photochromic materials with silica PLCs [5]. Fig. 13 shows a schematic view of our proposed optical switch. This silica-based optical switch on a silicon substrate has a Mach–Zehnder interferometer configuration with two 3 dB directional couplers, which are linked by two polymer clad waveguide arms of the same length. The refractive indices of the two polymer claddings were adjusted to that of the silica glass cladding. We could adjust the refractive index of the clad polymer to the silica glass cladding to verify the 2,2,2-trifluoroethyl methacrylate monomer content. One polymer cladding contained a photochromic compound (DA1) which was selected based on the result of our study of diarylethene photochromic compounds.

Fig. 14 shows the relation between the output power and irradiation time of our proposed switch with alternating UV and visible light irradiation. The phase shift is shown by Eq. (5) which represents the correlation between refractive index change and phase change.

$$\Delta \Phi_{pc} = 2\pi \, \Delta n_{eff} L/\lambda \ldots\ldots \qquad (5)$$

where $\Delta \Phi_{pc}$ is the phase change of propagating light, $\Delta n_{eff}$ is the effective refractive index change, $L$ is the arm length of the polymer cladding, and $\lambda$ is the wavelength of the propagating light. This Eq. (5) shows that a refractive index change leads to a phase change in the propagating light.

The light exposure provided the $\pi$ phase shift needed to turn the device from fully on to fully off. The insertion loss of the switch was − 8 dB and the crosstalk ratio was − 12 dB. A photochromic cladding refractive index change of 0.00014 was required for full switching. The switching time of our new switch is about 20–30 s. We are intending to use this new optical switch for repairing the route of an optical fiber. This kind of optical switch does not need to have a high switching speed. So our optical switch can be adopted for this use. For the construction of future optical communication systems, our switch can be modified to form a self-holding optical switch, a silica-based semi-fixed frequency filter, and a silica-based optical attenuator.

## 4. Conclusions

We studied photochromic reactions in a solid polymer film containing photochromic diarylethene derivatives in connection with their refractive index changes. The refractive index change of DA1 was 0.0005 per 10 wt.% in PFEMA. The iteration durability of the two diarylethene photochromic compounds was much better than that of BTTM. This may be explained by the fact that dehydrogenation occurred much more easily with BTTM than with the other two compounds. When we compare the two fluorocyclopentene photochromic compounds, the symmetrical compound, DA1, was better in terms of durability than the unsymmetrical compound, DA2. The number of cycles at which 80% of the initial optical density value remained, was about 300 for DA1, about 100 for DA2 and about 10 for BTTM.

We proposed and fabricated a self-holding Mach–Zehnder optical switch using a photochromic compound and a polymer mixture as polymer cladding. The refractive index change was sufficient for a full switching operation.

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