

Photocurrent detection from photochromic diarylethene film

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The photocurrent characteristics of a diarylethene (DAE) film were investigated. The photocurrents were attributed to the dissociation of electric carriers from the excited molecules in the DAE film. We demonstrated the on-off property of the photocurrent according to the isomerization state. Results reveal that the short-wavelength light corresponding to the high-energy absorption band of the colored DAE film generated higher carrier/photon efficiency than did the long-wavelength light corresponding to the low-energy absorption band. © 2004 American Institute of Physics.
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Photochromism is defined as a reversible transformation by photoirradiation between two isomers with different absorption spectra. The strong interest in photochromic materials has been increasing because they are promising candidates for ultra-high-density photon-mode optical memory or optical switching devices.¹⁻³ During photoisomerization, not only the absorption spectra, but also other molecular properties, such as refractive indices, dielectric constants, dipole moments, and electronic characteristics are changed reversibly. Recently, there has also been interest in changes in the electronic characteristics with respect to the isomerization reaction of photochromic diarylethenes (DAEs), and their applications.^{4,5} A particular type of organic semiconductor memory device with a DAE derivative, which utilizes the isomerization reaction of the DAE by electrical carrier-injection, has also been proposed.⁶

It is crucial to reveal the optical and electronic characteristics of photochromic DAE films in order to take full advantage of their applications in a variety of optical and electronic devices. In this letter, we investigate the photocurrent obtained from the DAE layer, which is attributed to electric carrier dissociation from photoexcited DAE molecules.

An organic dye molecule, in general, absorbs a photon and attains an excited state. In the case of photochromic DAEs, the excited molecules transform into another isomer with their photoisomerization quantum yield. The electron and hole in the excited molecule exist on the lowest unoccupied molecular orbital level and the highest occupied molecular orbital (HOMO) level, respectively. When an electric field is applied to the excited molecule, these carriers are able to dissociate from the molecule, thus returning the molecule to the ground state.

Carrier dissociation from electroluminescent molecules has also been reported.⁷ By using the carrier dissociation for photoexcited photochromic molecules, it is possible to control the photochromic reaction by applying an electric field due to the return of the excited molecule to the ground state. The dissociated carriers can be observed as an external photocurrent that is taken out via electrodes. If the irradiating-light wavelength is selected as the wavelength at which only one isomer has absorption, the photocurrent can be switched

according to its isomerization state. This indicates the feasibility of a photoswitchable light sensor.

Figure 1 shows the molecular structure and the absorption spectrum of the DAE derivative evaporation film used in our experiment. The uncolored open-ring state of the DAE film changes into the colored closed-ring state upon irradiation with ultraviolet light, and the colored state returns to the uncolored state upon exposure to visible light.

Figure 2 shows the device's structure and illustrates energy levels of the device. The DAE layer and the Mg_{0.9}In_{0.1} cathode layer were deposited, in turn, on the glass substrate with an indium tin oxide (ITO) anode by the vacuum-evaporation method. The thickness of the DAE layer was 100 nm and the area of cell was 4.0 mm². The DAE layer was initially colored by irradiating it with ultraviolet light. The absorption spectrum in Fig. 1 indicates that the colored-state film consisted of only closed-ring-state molecules, which was due to very low ring-opening quantum yield (below 10⁻⁴), and the uncolored film of only open-ring-state molecules. Visible light in the 400–800 nm region is absorbed by only the closed-ring molecules.

The diode characteristics were observed for the colored state; that is, when the ITO electrode was positively biased, current flow was observed, whereas no current flow was found for the negatively biased ITO electrode (reverse-bias

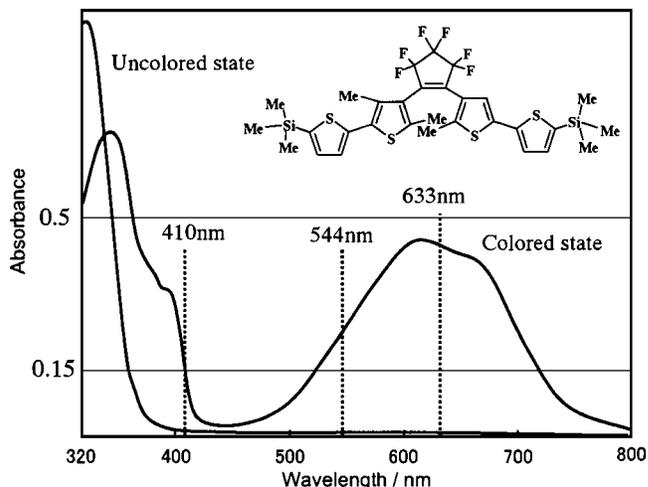


FIG. 1. Molecular structure and the absorption spectrum of the DAE derivative evaporation film.

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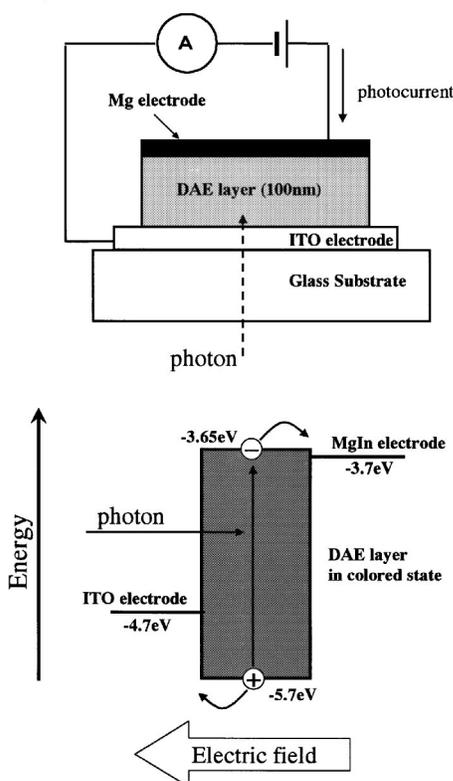


FIG. 2. Device structure and energy levels of the device.

condition). However, the cell in the uncolored state with the positively biased ITO electrode showed no current flow. These characteristics of electric carrier injection are consistent with our previous result.

Figure 3 shows the applied-voltage dependence of the photocurrent. In this case, the device was in the reverse-bias condition and no current was observed without light irradiation for both states. In addition, no current was observed when the device in the uncolored state was irradiated by 410 nm laser light, which corresponds to the result that no absorption was displayed by the uncolored DAE layer at 410 nm, either. On the other hand, there was a current observed for the colored state, which increased with the applied voltage.

Figure 4 shows the light-power dependence of the photocurrent. In this case, the device was in the reverse-bias

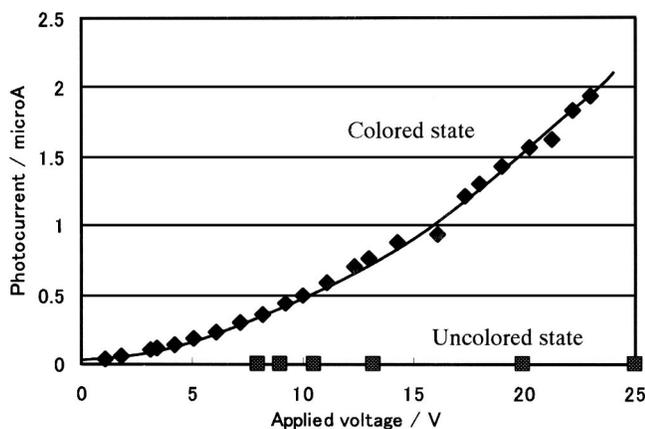


FIG. 3. Applied voltage dependence of the photocurrent. The device was reverse biased, and the laser power and the wavelength were 0.4 mW in the cell area and 410 nm, respectively.

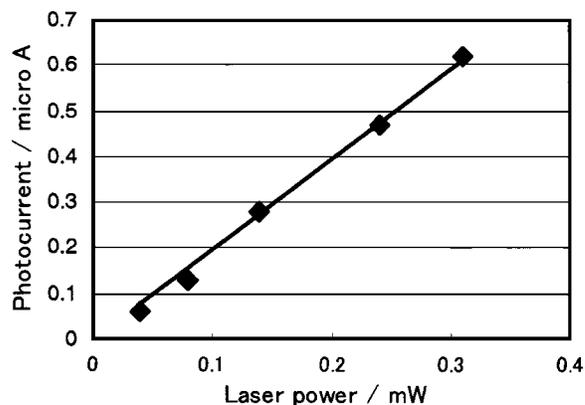


FIG. 4. Light-power dependence of the photocurrent. The device was in reverse-bias condition with the voltage 13 V. The wavelength of irradiating laser light was 410 nm and the absorbance at that wavelength was 0.15.

condition, with a voltage of 13 V and a 410 nm irradiating laser light obtained with a GaN semiconductor device. The laser's power was varied from 0.04 to 0.31 mW within the cell area. This figure shows that the observed current was increased linearly from 0.06 to 0.61 μ A proportional to the light power. It is certain, therefore, that the current was generated by light absorption in the DAE layer and that it originated from the dissociation of carriers on the excited molecules.

In order to investigate the mechanism of the photocurrent generated by carrier dissociation from the photoexcited DAE molecules, we measured the carrier/photon efficiencies for several wavelengths of irradiating light. Figure 5 shows the efficiencies that were calculated by taking into account the light absorbed by the DAE layer at these wavelengths, the reflectance of MgIn electrode layer, irradiating light power, and the number of photogenerated carriers obtained from the observed external photocurrent. We used lasers with wavelengths 410, 544, and 633 nm; the latter two lasers were oscillated from HeNe laser devices. The respective light powers of the 410, 544, and 633 nm lasers were 0.22, 0.10, and 1.30 mW/mm², respectively. The temperature dependence of the current was observed. The temperature dependence and the linearity of these plots for the carrier/photon efficiency given in Fig. 4 showed that the transport mechanism of photogenerated carriers corresponded to the Poole-

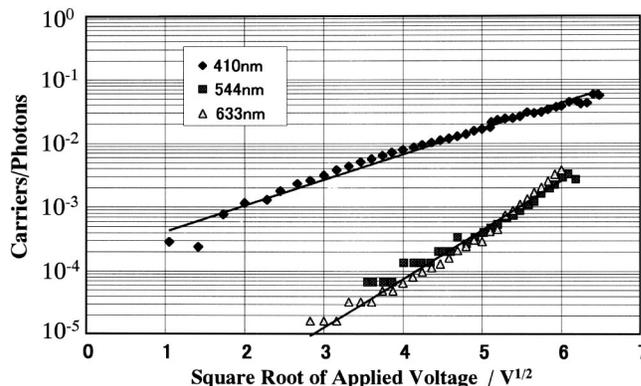


FIG. 5. Electric carrier/photon efficiencies. These were calculated by taking into account of the light absorption by the DAE layer at these wavelengths, the reflectance of MgIn electrode layer, irradiating light power, and the number of photogenerated carriers obtained from the observed external photocurrent.

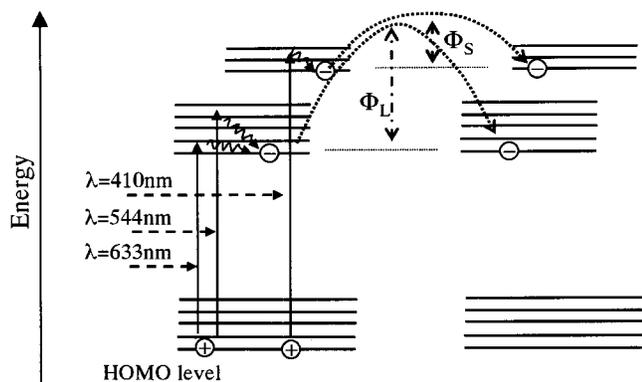


FIG. 6. Energy model for photoabsorption and carrier transportation by the hopping mechanism.

Frenkel effect, which is described in Eq. (1), as

$$\ln I \approx -\frac{\Phi}{kT} + \frac{\beta\sqrt{E}}{kT}, \quad (1)$$

where I , E , k , and T are the current, which is proportional to the efficiency in this case, the electric field proportional to the applied voltage, Boltzmann's constant, and absolute temperature, respectively. In addition, Φ corresponds to the potential barrier height between the molecules, β is a constant defined by $\beta = \sqrt{e^3 / \pi \epsilon \epsilon_0}$, where e is the elementary charge, ϵ a relative dielectric constant, and ϵ_0 a dielectric constant of the vacuum. The carrier transport model of photogenerated carriers in the colored DAE film is attributed to a hopping model with potential barriers between the closed-ring molecules.

In Fig. 6, the higher efficiency obtained with the 410 nm light than by 544, and 633 nm light excitation indicates that the electron energy level excited by 410-nm photons is higher than those by 544 and 633-nm photons, since the hole energy levels on the HOMO are to be the same for absorption of the different wavelength photons. Excited electrons at higher energy levels can move over lower-potential barriers easily and, therefore, cause a high electron-hole dissociation efficiency, as described by the Onsager model. The same efficiency for 544 and 633-nm photons, however, means that the photocurrent mechanism for the DAE film is not so simple. This is illustrated in the plots, which indicate that the electron energy levels for 544 and 633-nm photons are the

same, whereas the excited energy level of the 410-nm photons is different. The closed-ring state of diarylethenes, in general, displays two broad absorption bands, and these absorption bands absorb linearly polarized light differently from each other.⁸ This suggests there are two independent excited states, which correspond to different linearly polarized light absorptions and different energy levels, for the DAE molecule. Figure 6 shows an energy model for photoabsorption and carrier transportation that employs the hopping mechanism. This model shows that the low-energy absorption band ranging from 500 to 750 nm in Fig. 1 corresponds to the large-potential barrier Φ_L for excited electrons and contributes to a low photocurrent, whereas the high-energy absorption band at wavelengths shorter than 450 nm corresponds to a small-potential barrier Φ_S .

In summary, we investigated the photocurrent characteristics of diarylethene film. The photocurrent was attributed to the dissociation of electric carriers from the excited molecule. We also demonstrated the on-off property of the photocurrent according to the isomerization state. Results indicated that the photocurrent obeyed the carrier hopping mechanism, which is based on the Poole-Frenkel effect. Furthermore, we found that short-wavelength light corresponding to the high-energy absorption band of diarylethene film generated a higher carrier/photon efficiency than that of the long-wavelength light, which corresponded to the low-energy absorption band. Consequently, if the dissociation of electrons and holes from the excited molecule were to be applied to the control of the photoreaction, it would transform the excited molecule into a ground-state molecule.

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