Electrical carrier-injection and transport characteristics of photochromic diarylethene films

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Electrical carrier-injection and transport characteristics of photochromic diarylethene thin films were investigated. Injected and transported carriers (injected current) to the diarylethene film were increased with the existence ratio of the closed-ring form, which was one isomerization state of the diarylethene molecule. A dramatic increase was observed at a 12-percent existence ratio of the closed-ring molecules. A lowering effect of the potential barrier, which is caused by a Poole–Frenkel-like effect with a short distance interaction potential for hole transportation by increasing the existence ratio of the closed-ring molecules is proposed as the mechanism behind this phenomenon. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1634375]

Photochromic material is attracting great interest because it is a promising candidate for ultra-high-density optical memory media or optical switching devices.[1–5] Photochromism is defined as a reversible transformation between two isomers with different absorption spectra by photo-irradiation. During the 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, the electronic characteristic changes according to the isomerization reaction of photochromic diarylethenes and their applications have attracted interest.[6] One application is a nondestructive readout method of photon-mode optical memory using a photocurrent detection.[7] This method can nondestructively read memory recorded in an ultra-thin photochromic layer with a high signal-to-noise ratio.[8] Furthermore, a type of organic semiconductor memory device with a diarylethene derivative, which utilizes the isomerization reaction of the diarylethene by electrical carrier-injection, has also been proposed.[9]

Revealing the electronic characteristic of photochromic diarylethene films for their application to various electronic devices is indispensable. In this paper, we investigated the change in the carrier injection/transport characteristics with photoisomerization of a photochromic diarylethene film.

Photochromic diarylethenes show large ionization potential (Ip) changes with photoisomerization upon photoirradiation.[7,8] Open-ring state and closed-ring state molecules have an Ip of 5.7 eV and over 6.2 eV, respectively. The injection and transportation of electric carriers (holes) from anodes to the diarylethene layer can be controlled by the state of the diarylethene layer. When the layer is in the open-ring state, the potential barrier Φ between the anode (or hole transport layer) and the diarylethene layer is large and, therefore, it is difficult to inject the holes into the layer. On the other hand, when the layer is in the closed-ring state, the potential barrier Φ is small and holes are easily injected into the layer. This model is, however, quite simple and naive

because the colored film obtained by ultraviolet light irradiation is, in general, in a photostationary state and contains both isomers. The detailed carrier injection/transport mechanism of the diarylethene film must therefore be revealed.

Figure 1 shows the device structure used in our experiment. A diarylethene derivative (DAE) with triphenylamine groups, which showed high hole mobility, was used. N,N′-di(naphthalene-1-yl)-N,N′-diphenyl-benzidine (α-NPB) was used as the hole transport layer. The diarylethene layer, the NPB layer and Mg (magnesium) cathode layer were each deposited on the glass substrate with an Indium Tin Oxide (ITO) anode (Ip=4.7 eV) by the vacuum evaporation method in turn. The thicknesses of the diarylethene layer and the NPB layer were 50 nm and 30 nm, respectively. At first, the diarylethene layer was uncolored and consisted of only open-ring state molecules.

Voltage–current characteristics upon UV (ultraviolet) irradiation (365 nm, 4.0 mW/cm^2) are shown in Fig. 2. The current was gradually increased with the irradiation, and, therefore, with the increase of closed-ring state molecules. The photostationary colored state was obtained after 540 s of UV irradiation. The isomerization ratio for the photostationary state was 12%, which was obtained by measuring the absorption spectrum of the photostationary colored film under the same condition. The isomerization ratio of dia-
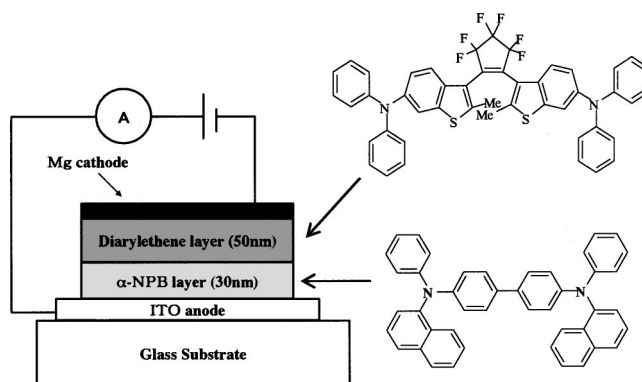

FIG. 1. Device structure and molecular structure of the diarylethene.
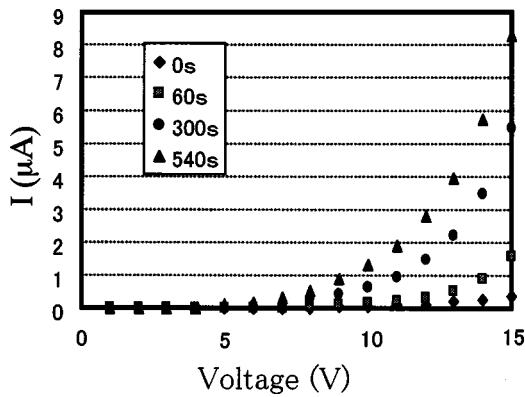
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Appl. Phys. Lett., Vol. 83, No. 24, 15 December 2003

T. Tsujioka and K. Masuda   4979

FIG. 2. Voltage-current characteristics upon uv irradiation.

FIG. 4. Absorbance dependence of the current. The existence ratio of closed-ring molecules is proportional to the absorbance (Abs) at the wavelength of 600 nm, in which only closed-ring molecules shows absorption.

rylethene derivatives is strongly dependent on their molecular structure, the light wavelength and other experimental conditions. In general, the ratio is high for solution samples or polymer dispersed film samples, but the ratio for some pure diarylethene films becomes relatively low. The temperature dependence of the photostationary colored film current was observed. The carrier injection/transport mechanism was thus attributed to a Schottky-type mechanism [including the Poole–Frenkel (P–F) effect]. This type of mechanism is described by the following equation:

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

where I, E, k, and T are the current, the electric field that is proportional to the applied voltage, the Boltzmann's constant and the absolute temperature, respectively. β is a constant determined by the elementary charge, a relative dielectric constant and a dielectric constant of the vacuum.

Figure 3 shows the $\log(I)$-square root of the voltage plot of the change of voltage–current characteristics upon UV irradiation. The parallel shift of a straight line upon UV irradiation indicates that the current transport/injection mechanism obeys Eq. (1), in which the potential barrier Φ apparently changes upon irradiation.

In order to investigate the relation between the potential barrier height and the existence ratio of closed-ring molecules in the film, the absorbance dependence of the current was measured. The existence ratio is proportional to the absorbance (Abs) at the wavelength region, in which only closed-ring molecules show absorption. Figure 4 shows the Abs dependence of the current at a 600-nm wavelength. The
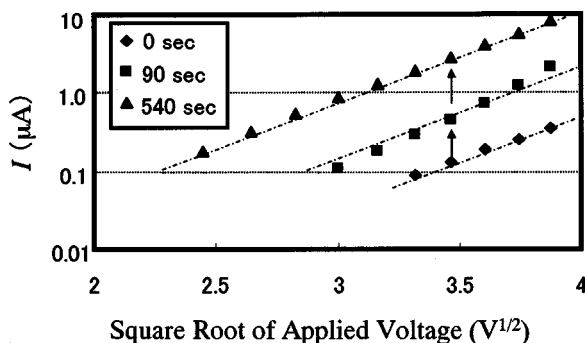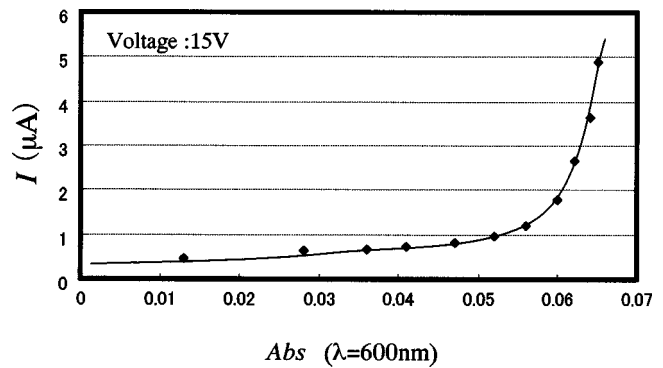
current level was very low in the low existence ratio region corresponding to Abs<0.06. The current, however, increased dramatically at Abs>0.06. The photostationary state corresponded to Abs=0.065 and the existence ratio of the closed-ring molecules was 12%.

Since the colored DAE layer consists of a mixture of closed-ring and open-ring molecules, the potential model of the layer is complicated. The closed-ring molecules have a smaller ionization potential than that of the open-ring molecules and the existence ratio of closed-ring molecules is low. Therefore, the closed-ring molecules act as carrier traps for hole transportation. In such a case, the carrier transport mechanism is described by the P–F mechanism. It is well known that, in general, the effective Coulomb potential for a P–F current is proportional to $1/r$, where r is the distance between the carrier and the trap. The lowering effect of the potential barrier Φ with an increase in the existence ratio of closed-ring molecules can be regarded as the superposition effect of potentials formed by neighboring traps of closed-
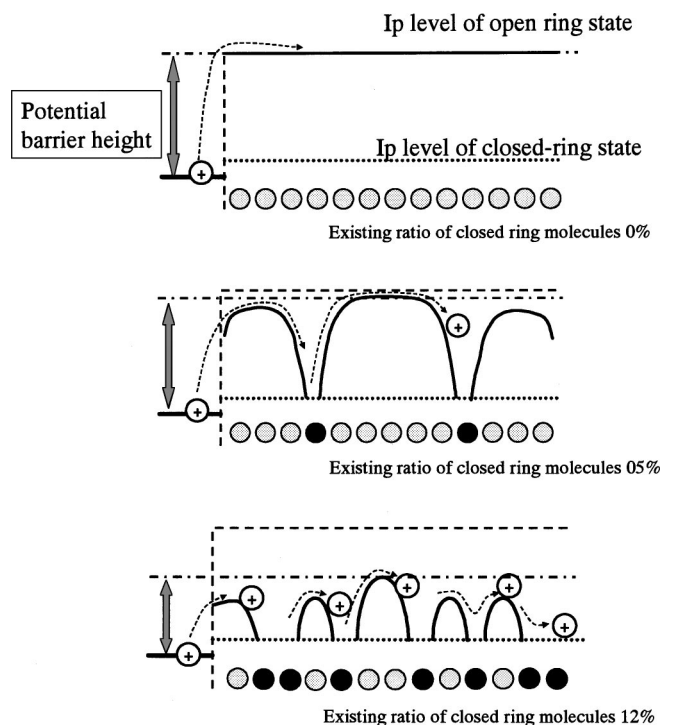

FIG. 3. Log(I)-square root of voltage plot of the change of voltage–current characteristics upon uv irradiation.

FIG. 5. Model for lowering effect of the potential barrier Φ with increasing the existence ratio of closed-ring molecules.

ring molecules, as shown in Fig. 5. For example, 0.12 (12%) of the three-dimensional existence ratio of closed-ring molecules corresponds to $\sqrt[3]{0.12} \approx 0.5$ (50%) of the one-dimensional existence ratio in the direction of layer thickness. Furthermore, the dramatic increase around Abs=0.06 of the current indicates that the potential form is not a long distance interaction such as $1/r$, but a short distance interaction such as the Yukawa potential including an exponential extinction factor with distance r. The exact potential form, however, is unknown. Such a shielding effect of interaction would be attributed to the existence of π electrons of the molecules.

In summary, the electrical carrier-injection and transport characteristic of photochromic diarylethene thin film were investigated. The injected current was dramatically increased at a closed-ring molecule existence ratio of 12%. This was attributed to the lowering effect of the potential barrier, which was caused by a Poole–Frenkel-like effect with a short distance interaction potential for hole transportation by an increasing existence ratio of closed-ring molecules.

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