

## Organic bistable memory characteristics with a photochromic diarylethene layer

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(Received 29 April 2005; accepted 20 September 2005; published online 18 November 2005)

Device structure dependence of the recording efficiency of organic bistable molecular memory using photochromic diarylethene (DAE) was studied. Devices with a thicker memory layer showed faster current decrease, that is, shorter writing time. This was attributed to effective isomerization at the many carrier traps in the memory layer. The device with an electron transport layer that consisted of a Silole derivative showed fast writing speed. The device with an Alq3 electron transport layer showed electroluminescence. This indicates the holes were transported through the DAE layer without contribution for isomerization. DAE molecules with good receptivity for both carriers should be developed for obtaining high speed memory. © 2005 American Institute of Physics. [DOI: 10.1063/1.2133913]

Photochromic memory has been of interest over a decade because it is a promising candidate for ultrahigh-density optical memory media or optical switching devices.<sup>1-4</sup> Photochromism is defined as a reversible transformation between two isomers with different absorption spectra upon photoirradiation. During photoisomerization not only the absorption spectra but also other properties, such as refractive indices, dielectric constants, and electronic characteristics are changed reversibly. Photochromic diarylethenes with heterocyclic rings (DAEs) are well known to have the following characteristics: good thermal stability for both isomers (bistability); high fatigue resistance; and rapid response.<sup>1</sup> Their open-ring form (uncolored form) absorbs a photon in the ultraviolet region of the optical spectrum, and yields closed-ring form (colored form) with a different spectrum. This closed-ring form absorbs a photon in the green-red region of the visible spectrum and returns into the open-ring form.

Recently, the electronic characteristics change according to the isomerization reaction of DAEs and their applications to organic electronics have been of interest.<sup>5-7</sup> A principle for an organic semiconductor memory device has been proposed for constructing a nonvolatile, ultrahigh-density and extremely low-power consumption memory device.<sup>7</sup> The principle of this memory device is based on a reversible isomerization reaction of the bistable DAE molecule by electric carrier injection. This is achieved by excitation by encountering a hole injected from the anode and an electron injected from the cathode on the bistable molecule, not by photoexcitation. The electron on the lowest unoccupied molecular orbital level and the hole on the highest occupied molecular orbital level of the molecule produce an excited state identical to that produced by photoexcitation, so the molecule is transformed into another isomerization form. In the case of the DAEs, ionization potential  $I_p$  of the molecule is changed according to its isomerization form. The closed-ring form has  $I_p$  of 5.7 eV and the open-ring form has more than 6.2

eV.<sup>5,7</sup> Information readout is achieved by detecting the electric current through the molecules affected by the difference of  $I_p$ .

Carrier encounter efficiency should be improved to obtain high speed memory device. In this article, the device structure dependence of writing speed is investigated. As the efficiency of organic electroluminescence device is improved by adopting a multilayer structure with a hole transport layer and an electron transport layer as well as an emitting layer, the effect of electron transport layer for this memory device is discussed.

Figure 1 shows the device structure. The DAE derivative with triphenylamine groups, which showed high hole mobility, was used as a memory layer. 4,4', 4''-Tris(N-3-methylphenyl-N-phenyl-amino)-triphenylamine (MTDATA) and N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine ( $\alpha$ -NPB) were used as the hole injection and transport layers, respectively. The DAE layer as the memory layer (ML), the  $\alpha$ -NPB layer and Mg<sub>0.9</sub>In<sub>0.1</sub> cathode layer were deposited on the glass substrate with an indium tin oxide (ITO) anode ( $I_p=4.7$  eV) by the vacuum evaporation method, in turn. The thicknesses of MTDATA and  $\alpha$ -NPB layers were 10 and 70 nm, respectively. The device area was 4 mm<sup>2</sup>. Various DAE layer thicknesses were adopted and the writing speed, which was defined by the half decrease time of the current, was measured. The initial state of the memory layer was colored photostationary state, obtained upon irradiation of the ultraviolet light with the wavelength of 365 nm. The concentration of closed-ring isomer of the initial state was 10 mol %, which was independent of the thickness of the ML because of the photostationary state. The conversion efficiency from closed form to open form is related to the quantum yield of photoisomerization reaction and the usual photoreaction quantum yield for the DAE is 0.1 at the wavelength of 633 nm.

Figure 2 shows the current decrease characteristics for various memory layer thickness devices. The half decrease time of the normalized current was 8, 20, and 40 s for

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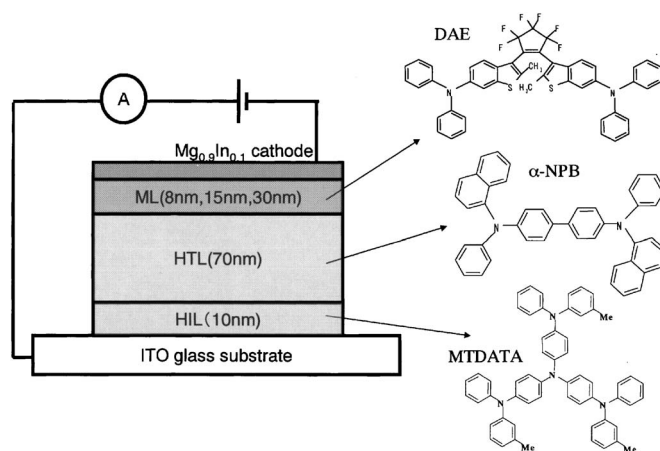


FIG. 1. Device structure of the organic memory device.

memory layer thickness of 30, 15, and 8 nm devices, respectively. Writing time, therefore, was shortened by increasing the memory layer thickness. Furthermore, the initial current values for each device were 370, 800, and 950  $\mu\text{A}$  for thickness of 30, 15, and 8 nm devices, respectively. This result means thicker memory layer device showed shorter recording time in spite of smaller injected current.

Figure 3 shows a replot using a vertical axis with observed current for the results of 8 and 30 nm thick devices. The hatched areas correspond to the total injected carriers to obtain half decrease. This shows that for writing, the 8 nm device needs 12-time carrier injection compared to the 30 nm device. In general, thicker memory layer requires more reacted molecules to change the electronic property of the entire memory layer, that is, more electric carriers. However, our experimental results refute such a naive conception.

This contradiction on the surface can be solved by considering the following potential model as shown in Fig. 4. The initial state was obtained upon UV light irradiation, and the open-ring molecules in the layer convert to closed-ring molecules. As a result, the simple description illustrates that the ionization potential level of the memory layer changed from an open-ring to a closed-ring state. However, this description is too simplistic, and the potential level for the real memory layer is more complicated. The convert ratio from open-ring to closed-ring states for photochromic molecules upon UV irradiation in the memory layer does not always equal 100%. The convert ratio for this experimental case was

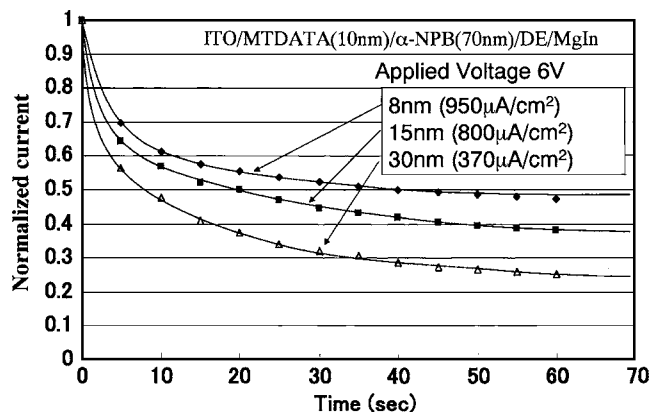


FIG. 2. Current decrease characteristics (normalized) depending on the memory layer thickness for the device shown in Fig. 1.

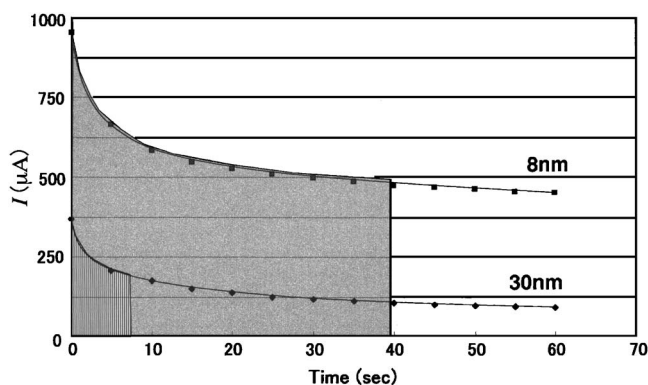


FIG. 3. Comparison of total carriers injected to the devices.

about 10 mol %, so the real potential shape in the DAE layer is the shape having many carrier traps that corresponds to the closed-ring molecules in open-ring molecule ground, as shown in Fig. 4. The holes injected into the memory layer are trapped on these closed-ring sites and encounter electrons injected from the cathode, and then the closed-ring molecules are transferred to the open-ring molecules. Since the thick memory layer contains many carrier traps, it is easy to cause isomerization reactions and to form potential barriers for the holes. This indicates that the current for the thick memory layer would be reduced rapidly. On the other hand, the many holes moving through the thin memory layer are transported without encounter to the electrons because of the lack of carrier-trap sites. This causes the current for the thin memory layer to reduce slowly.

The effect of electron transport layer (ETL) was also investigated. The device structure is shown in Fig. 5. The ETL was Silole derivative (PyPySPyPy) (Ref 8) or Alq3 which was a conventional electron transport material. The materials used in other layers were the same as in Fig. 1. Figure 6 shows the characteristics of current decrease for the memory device with and without a Silole derivative ETL. Apparently, the device with the electron transport layer indicates current decay three times faster than the device without ETL. This attributes to effective electron transport to the memory layer from the cathode.

On the other hand, the device with the Alq3 electron transport layer does not show marked effects, and electroluminescence from the Alq3 layer was observed. This result means that the holes were moving through the DAE layer

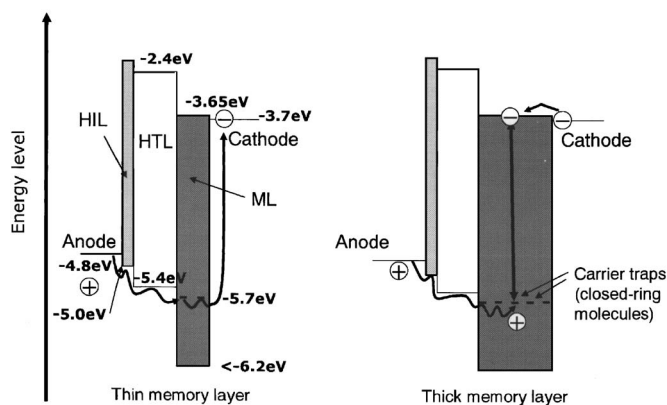


FIG. 4. Potential model describing the origin of the writing efficiency difference depending on the memory layer thickness.

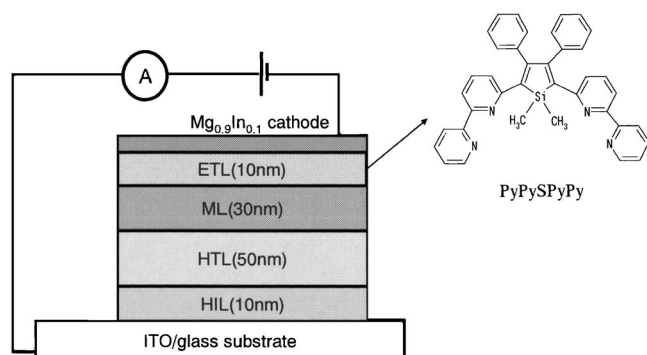


FIG. 5. Structure of the device with an electron transport layer.

without contribution for isomerization and recombined with the electrons in the Alq<sub>3</sub> electron transport layer. Our results indicate that the DAE molecule has good hole transport property but poor electron receptivity, so DAE molecules with good receptivity for both carriers should be developed for obtaining high-speed bistable molecular memory.

In summary, the device structure dependence of writing speed, for the bistable molecular memory using the DAE memory layer was investigated. The device with the thicker memory layer shows faster current decrease time. In order to obtain the high-speed memory, the DAE molecules with the good both-carrier receptivity should be developed.

Part of this study was supported by Grant-in-Aid for Scientific Research from Japan's Ministry of Education,

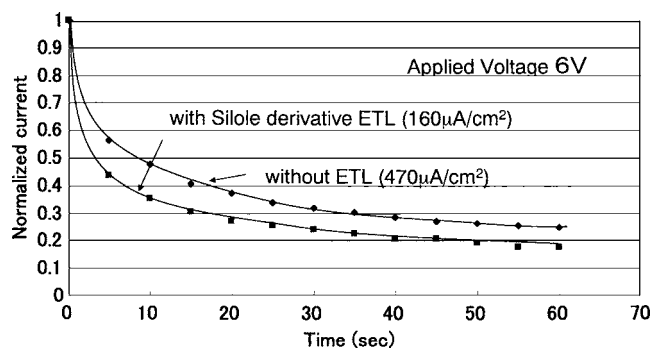


FIG. 6. Current decrease characteristics (normalized) of the memory device with a electron transport layer.

Culture, Sports, Science and Technology. We would like to acknowledge the Chisso Corp. who supplied the Silole derivative.

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