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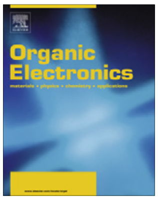

Nonvolatile organic memory based on isomerization of diarylethene molecules by electrical carrier injection

Tsuyoshi Tsujioka *, Toshiyuki Sasa, Yasuhiro Kakihara

Osaka Kyoiku University, Asahigaoka 4-698-1, Kashiwara, Osaka 582-8582, Japan

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ABSTRACT

A novel organic memory principle is proposed. The photochromic diarylethene (DAE) memory layer was isomerized to the colored state from the uncolored state by electrical carrier injection, and a high ON–OFF ratio of 100 was achieved. The recording time can be dramatically shortened by increasing voltage. The current percolation path consisting of colored molecules was generated in the recording process, and thermal degradation of the recorded state occured. The origin of the degradation was revealed: diffusion of the colored molecules to the uncolored DAE matrix with low glass transition temperature (Tg). The adoption of high-Tg DAE would enable memory with a high ON–OFF ratio and excellent stability.

1. Introduction

Organic electronics devices such as light emitting devices, thin film transistors and solar cells have attracted considerable attention because of their low production cost and flexibility [1,2]. Organic semiconductor memory is indispensable as an important element for information processing as well as transistors. Various memory principles including ferroelectric [3], filamentary structure of metal nanoparticles [4] and floating gate types [5] have been proposed. One of such devices has a structure with metal nanoparticles [6,7], in which electrical charges are stored. An essential problem for the charge storage type memory is insufficient information retention caused by charge leakage [5,6,8,9].

Another memory principle introduced here uses electrical isomerization of photochromic diarylethene (DAE). DAEs are well known as a series of photochromic molecules with low fatigue in reversible isomerization and very high stability in both isomerization states [10]. Electrical function of DAEs has attracted interest [11] but almost all studies have been on photoswitching of electrical current [12–17]. The colored (closed-ring) state of DAE has an ionization potential (Ip) of 5.7–5.8 eV and an open-ring molecule over 6.2 eV, and the difference of Ip induces a change of current injection into the DAE layer [18]. The recording principle of semiconductor memory using DAE has been attained by electrical carrier injection [19,20]. The excited state generated by carrier injection, in which a hole is on the HOMO level and an electron on the LUMO level, causes isomerization (ring-opening, RO) reaction and the ionization potential of DAE changes. Information readout utilizes a change of injected current based on a difference of a potential barrier between the work function of the electrode and Ip of the DAE layer. Memory with DAE molecules, therefore, has the potential for long retention time. The ON–OFF ratio between the recorded state and unrecorded state, however, was low because both states are current conduction states; it was below 10 times [19,21].

2. Principle and experimental

The novel principle proposed here utilizes a ring-closure (RC) reaction by carrier injection as a recording mode. Fig. 1 illustrates the recording principle of RC mode by electrical carrier injection. The unrecorded state of the DAE layer consists of uncolored open-ring molecules.

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* Corresponding author. Tel./fax: +81 72 978 3633.
E-mail address: tsujioka@cc.osaka-kyoiku.ac.jp (T. Tsujioka).

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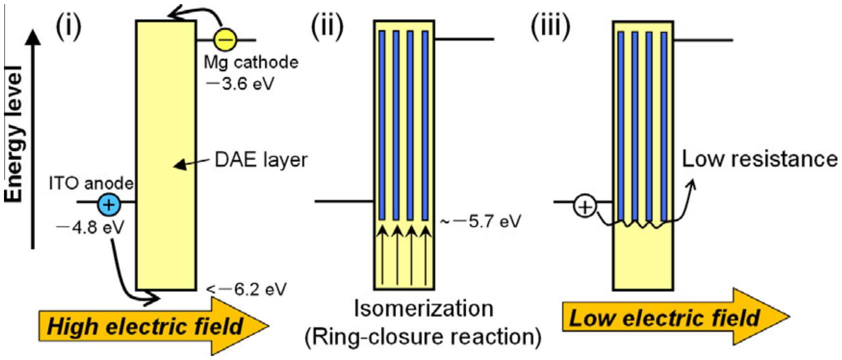

Fig. 1. Recording principle of memory device with diarylethene layer by electrical carrier injection.

Electric carriers (holes and electrons) are injected from the electrodes beyond a large potential barrier by applying relatively high voltage. Electrical carrier injection to the uncolored DAE molecules creates an excited state, in which an electron is on the LUMO level and a hole on the HOMO level of the uncolored molecule, inducing the RC reaction to open-ring molecules in the layer. The unrecorded state is in a hard current-flow state, while the recorded state is in an easy current-flow state. When the current difference between the unrecorded and recorded states is detected by applying a low voltage for information readout, a large ON–OFF ratio is achieved.

Fig. 2(a) illustrates excitation of a DAE molecule by carrier injection. The DAE molecule with benzothiazole bases was newly designed because a benzothiazole basis shows good electron affinity [22]. In general, lots of organic molecules including DAEs have hole transport ability [23,24]; therefore, a DAE molecule with an electron affinity basis would be expected to easily make both carrier acceptance capabilities, which means it is easy to make an excited state for isomerization. The memory device structure shown in Fig. 2(b) was prepared by a conventional vacuum evaporation method. Glass substrates with ITO electrodes were cleaned by ultrasonication in acetone and then by using a UV-ozone cleaner. A Cu-phthalocyanine (CuPc) layer (thickness: 10 nm) as a hole injection layer and DAE layer (thickness: 40 nm) as a memory layer were deposited on the ITO substrate using vacuum evaporation under 1×10^{-5} Torr at room temperature (25 °C). The Mg cathode (thickness: 70 nm) enables easy electron injection into the organic layer. The deposition rates and thicknesses were controlled by a quartz thickness monitor during vacuum evaporation. The cell area was 2×2 mm^2. The isomerization state of the DAE layer as deposition was in the uncolored open-ring state. The amorphous DAE film prepared by vacuum evaporation showed good photochromism (see SI). *I*–*V* measurement was measured in dried N_2 atmosphere.

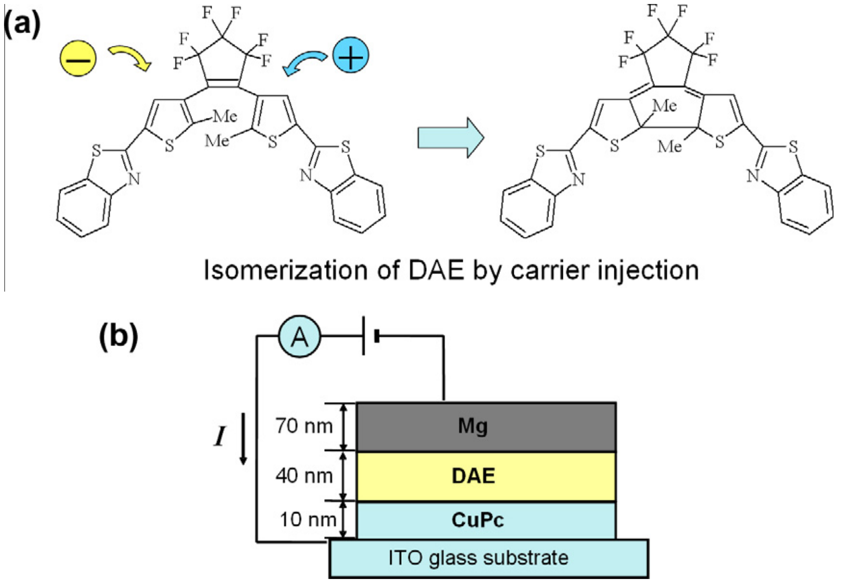

Fig. 2. (a) molecular structure of DAE and illustration of isomerization by carrier injection. (b) Memory device structure. Cell area was 2×2 mm^2.

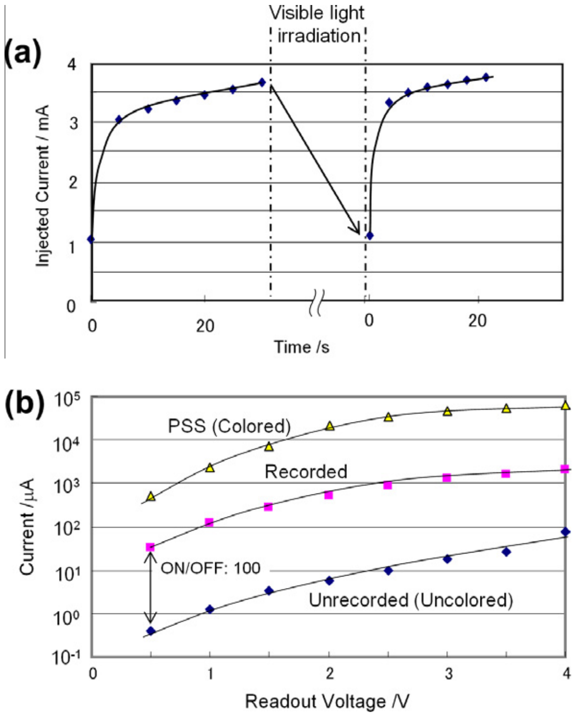

Fig. 3. (a) Changes of injected current. (b) Readout voltage dependence of ON–OFF ratio.

3. Results and discussion

First, we investigated a change of injected current into the uncolored DAE layer at a constant voltage of 7.5 V. Fig. 3(a) shows a change of current. The current was gradually increased with time from 1 mA at the unrecorded state to 3.6 mA after 30 s (recorded state). The recorded state did not change after several minutes under the dark condition and was recovered to the unrecorded state by visible light irradiation. This means that the change of current was caused by the RC reaction. (When the RO mode for recording is adopted, the current decreases and is recovered by UV light irradiation [17].)

Fig. 3(b) shows the readout voltage dependence of current levels in the recorded state obtained by applying voltage of 7.5 V for 30 s and in the unrecorded state. The current level of the photostationary state (PSS) obtained by UV irradiation is also displayed as a reference. The ON–OFF ratio was defined by a ratio of the current levels obtained by applying the low readout voltage to the unrecorded and recorded states. The ON–OFF ratio of 100 was achieved in a wide voltage range of 0.5–3 V. The high ON–OFF ratio at low voltage means that the memory with a coexistence of an excellent SNR and low power consumption at the readout process is possible. The ON–OFF ratio for the PSS was much higher than that by electrical recording. This suggests that the ratio of the colored molecules in the recorded state is very low. This will be discussed later.

The result shown in Fig. 3(a) indicates recording of the memory device requires carrier injection for comparably long time. Practical memory, however, has a very short recording time. Therefore, we investigate applied voltage dependence of the recording time to shorten the recording time (Fig. 4(a)). When the recording voltage (V_{rec}) was 7 V, the current increased gradually from 0.13 mA to 1.56 mA after 150 s. However, the current increased rapidly from 0.61 to 10.8 mA after 120 s for the voltage of 8 V and from 7.3 to 14.3 mA after 9 s for 9 V. The speed of current

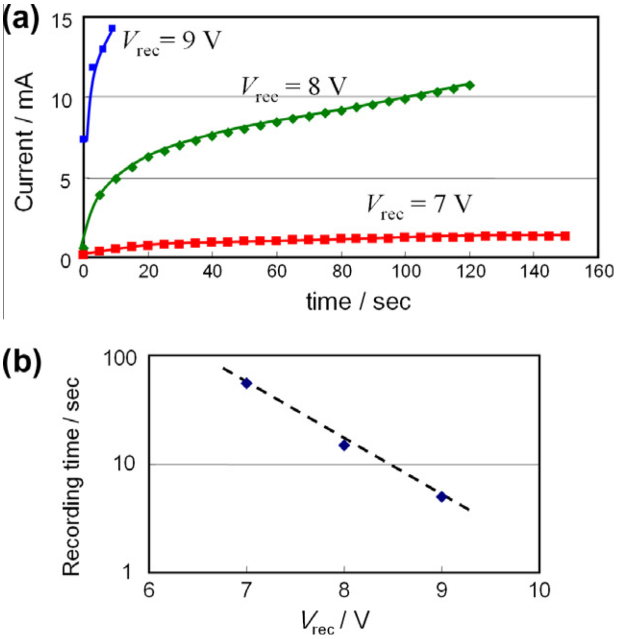

Fig. 4. (a) Changes of injected current depending on voltage. (b) Applied voltage dependence of recording time that achieved ON–OFF ratio of 100.

increase was dramatically improved by increasing the recording voltage.

To check the recording efficiency depending on the applied voltage, the recording time to achieve the same ON–OFF ratio was examined. Fig. 4(b) shows the voltage dependence of recording time to achieve the ON–OFF ratio of 100 at readout voltage of 0.5 V. Recording voltage of 7 V required 55 s, whereas the time was dramatically shortened to 5 s by increasing voltage from 7 to 9 V. This result means much shorter time would be achieved by adjusting the recording voltage.

To test the stability of stored information, repeated readout was carried out by applying pulsed voltage to the unrecorded state and recorded state, and the injected current was observed. Fig. 5(a) shows the applied voltage waveform and corresponding current for the unrecorded and recorded states (ON–OFF ratio: 100 at 0.5 V). The horizontal and vertical axes are time and voltage/current levels, respectively. The current pulse corresponding to the voltage pulse (pulse width: 1.6 ms, pulse frequency: 100 Hz) was observed for the recorded state, while no current pulse was observed for the unrecorded state.

Fig. 5(b) shows a change of each signal current level: the horizontal axis indicates readout cycles, and the corresponding time is also displayed. The vertical axis is normalized by the initial current level of the recorded state. No change of the signal level for the unrecorded state was observed even after 10^7 readout cycles but the level for the recorded state was decreased after 10^5 cycles (or 10^3 s). There are two possibilities for the signal degradation in the recorded state: the destructive readout (isomerization), or the low retention despite excellent thermal stability of the colored isomerization state of the DAE molecule (see SI).

To clarify which possibility causes the degradation of the signal level, we compared the repeated readout (at 0.5 V) with pulse frequency of 100 Hz and 10 Hz. If the destructive readout is an origin of the signal degradation, no difference in the degradation between 100-Hz and 10-Hz readouts must be observed with readout cycles. Fig. 5(c) shows the readout cycle dependence of the signal levels for the 100-Hz and 10-Hz readouts. The 100-Hz readout enabled more readout cycles than the 10-Hz readout. The discrepancy of readout cycle dependence means that the degradation is not due to undesirable isomerization in the readout process (destructive readout). Fig. 5(d) with readout time on the horizontal axis is a replot of Fig. 5(c). Apparently, the 100-Hz readout accelerates the degradation compared with the 10-Hz readout. Shorter retention in the 100-Hz readout suggests that the degradation is due to a thermal effect by frequent current injection.

Next, to show the degradation caused by the thermal effect more clearly, we investigated the temperature dependence of the degradation. Fig. 6(a) compares the degradations of the signal level in the 100-Hz readout for the recorded state stored at the temperature of 25 °C (room temperature) and 50 °C. The degradation at 50 °C was dramatically accelerated compared with that at 25 °C. This result means that the degradation in time for the recorded state is a thermal effect despite the excellent thermal stability of the colored molecule.

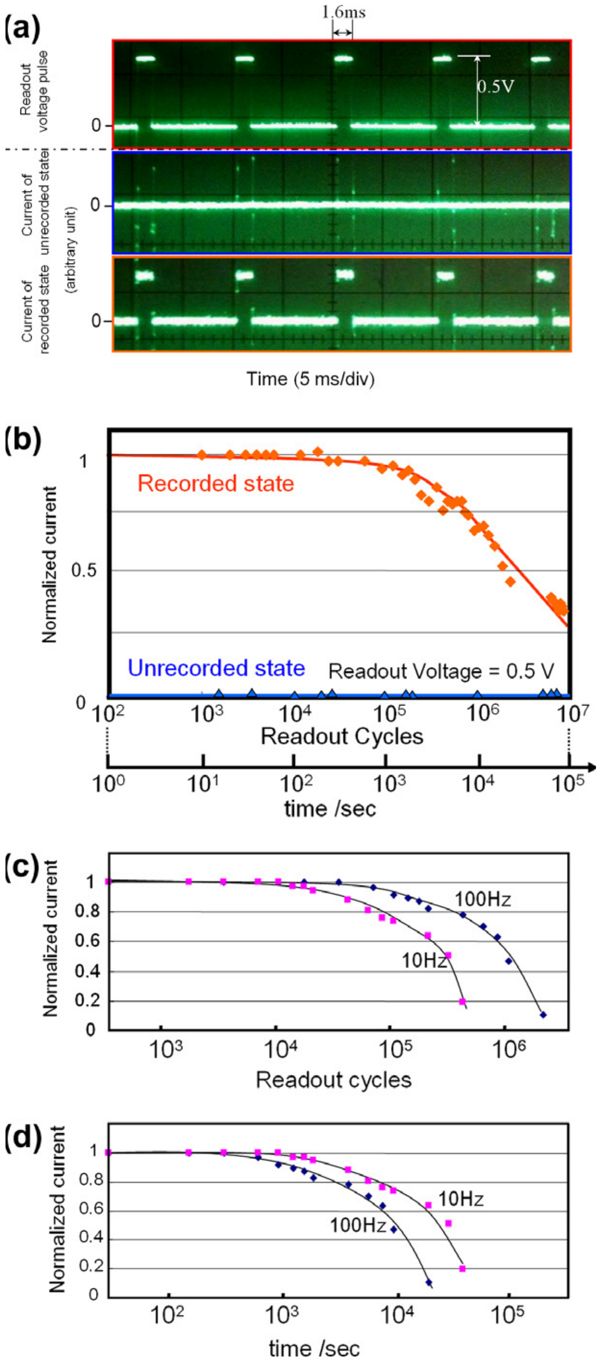

Fig. 5. (a) Voltage and current pulses in repeated readout. (b) Changes of readout signal pulse level. (c) Changes of readout signal level. Horizontal axis is readout cycles. (d) Changes of readout signal level. Horizontal axis is readout time.

Fig. 6(b) illustrates a recording process and a cause of the thermal degradation. Since a slight change in absorption in the DAE layer by recording with electrical carrier injection was observed, the ratio of colored molecule is

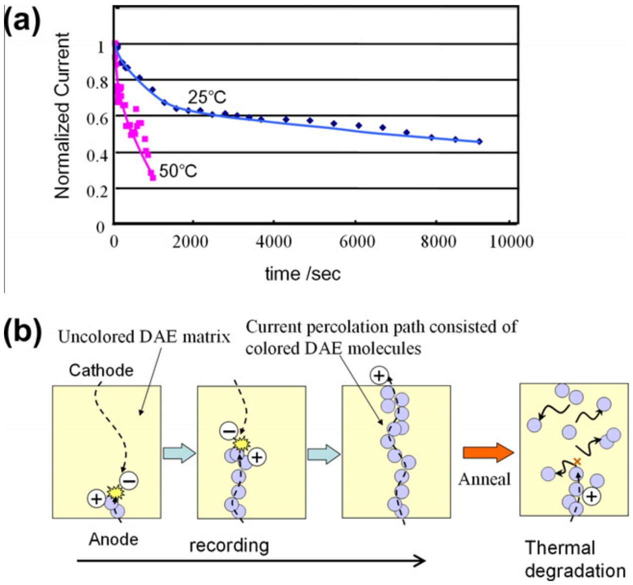

Fig. 6. (a) Temperature dependence of signal level in recorded state. (b) Models of recording process based on current path formation and thermal degradation caused by diffusion of colored molecules into uncolored DAE matrix with low Tg.

very low. The injected current level in the recorded state was very low compared with that in the photostationary colored state (Fig. 3(b)). These results suggest that the recording is achieved by generating the current percolation path consisting of the colored molecules. Electron and hole are encountered at the end of the incomplete path when carriers are injected into the DAE layer, isomerization occurs at the end of the path because holes are conducted on the colored molecules easily, and the path grows. Once the path connects both electrodes, the current flows only through the path and further isomerization does not occur around the path. This causes a low isomerization ratio of the recorded state. The path consisting of the colored molecules is surrounded by the many uncolored molecules, which consist low-Tg (79 °C, see SI) matrix. When the recorded state sample is annealed at high temperature, the colored molecules in the path diffuse into the uncolored low-Tg matrix, and the path is destroyed, as shown in the right side of Fig. 6(b). This is the reason for the thermal degradation. To achieve thermally stable memory, the DAE with high Tg in the uncolored state should be adopted.

4. Conclusion

In conclusion, a novel organic memory principle using the photochromic molecule, which was designed to have both carrier mobility, was proposed. The DAE molecules were isomerized to the colored state from the uncolored state by electrical carrier injection. The recording time can be dramatically shortened by increasing voltage. The high ON–OFF ratio of 100 was successfully achieved. The recording was achieved by generating the current percolation path consisting of the colored molecules in the uncolored matrix. The origin of the thermal degradation was revealed: diffusion of the colored molecules to the uncolored DAE matrix. The adoption of high-Tg DAE would enable memory with a high ON–OFF ratio and excellent stability.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2012.01.017.

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