

Hole-injection isomerization of photochromic diarylethene for organic molecular memory

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Hole-injection recording of organic semiconductor memory with a photochromic diarylethene memory layer was investigated by using a device structure with an electron block layer (EBL). Devices with thicker EBL showed faster current decrease, that is, high isomerization efficiency. The high efficiency of isomerization originating from the long lifetime of a cationic state was achieved by hole injection with low voltage. Hole-isomerization recording has the potential for very low power consumption organic memory. © 2006 American Institute of Physics.

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Organic electronic devices have been studied recently because such very cheap, small, and disposable electronic chips will be required for ubiquitous computing in the near future.¹⁻⁴ Organic memory is essential for organic devices as well as organic transistors, switches and antennas. Photochromic molecules are one of the most promising materials for obtaining bistable organic semiconductor memory. Photochromism is defined as a reversible transformation between two isomers with different absorption spectra upon photoirradiation.^{5,6} During photoisomerization not only such optical properties as the absorption spectra and refractive indices but also such electronic properties as ionization potential and dielectric constant are changed reversibly. Photochromic materials have been garnering interest for over a decade because so far they are the most favorable candidate for ultrahigh density optical memory media or optical switching device materials. Recently, changes of the electronic characteristics, based on the isomerization reaction of photochromic molecules, have received attention in the fields of organic molecular electronics and photonics.⁷⁻¹²

Photochromic diarylethenes (DAEs) with heterocyclic rings are well known to have the following characteristics: good thermal stability for both isomers, high fatigue resistance in isomerization, and rapid response.⁶ Their open-ring form (uncolored) absorbs a photon in the ultraviolet region of the optical spectrum and yields a closed-ring form (colored) with a different spectrum. This closed-ring form absorbs a photon in the visible region and returns to the open-ring form.

A principle for organic semiconductor memory has been proposed for constructing a nonvolatile, high density, low

power consumption memory device.¹³ The memory principle is based on an isomerization reaction of the bistable DAE molecule by electric carrier injection. This was achieved by excitation by encountering a hole injected from the anode and an electron injected from the cathode on the DAE 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 DAE, ionization potential I_p of the molecule is changed based on 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.^{11,13} The information readout was achieved by detecting the electric current through the molecules and the current is affected by the difference of I_p .

Isomerization reaction via a cationic state for several kinds of the DAE in solution by using electrochemical method, not via photoexcited state, has been reported.¹⁴⁻¹⁸ This suggests the feasibility of realizing efficient isomerization and information recording, based on hole injection into the DAE solid memory layer. The encounter of a hole and an electron for generating excited molecules means the disappearance of both carriers, but a transporting hole in molecules is conserved, which would convert many closed-ring molecules to open-ring form. In this letter, the possibility of the isomerization of DAE via the cationic state in the solid memory layer by hole injection is studied.

Figure 1 shows the device structure. DAE derivative with triphenylamine groups, which showed high hole mobility,¹¹ was used as a memory layer (ML). 4,4',4''-Tris (*N*-3-methylphenyl-*N*-phenyl-amino)-triphenylamine and *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (NPB) were used as a hole-injection layer (HIL) and a hole transport

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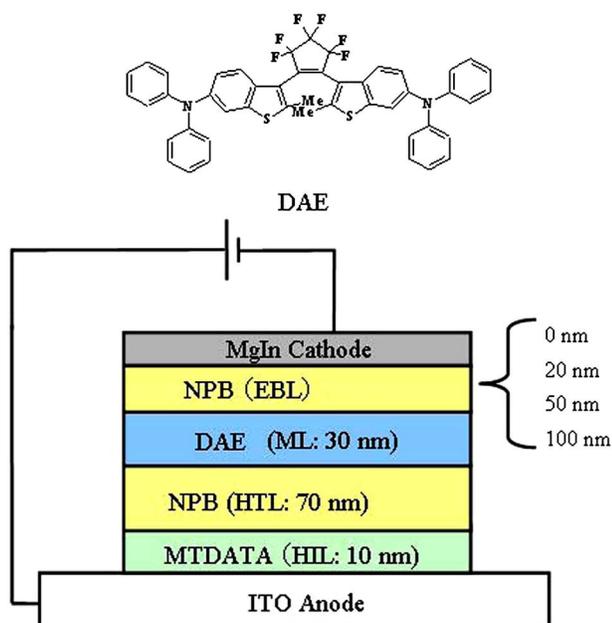


FIG. 1. (Color online) Device structure of organic memory device with an electron blocking layer.

layer (HTL), respectively. An additional NPB layer was also used as an electron block layer (EBL). HIL, HTL, ML, EBL, and $\text{Mg}_{0.9}\text{In}_{0.1}$ cathode layer were deposited on the glass substrate with indium tin oxide anode ($I_p=4.7$ eV) by vacuum evaporation method under the pressure of 5.0×10^{-6} Torr by turns. The HIL, the HTL, and the ML were set to be 10, 70, and 30 nm thick, respectively, but a variety of EBL layer thicknesses was adopted. The device area was 4 mm^2 . The initial state of the memory layer was a colored photostationary state, obtained upon irradiation of the ultraviolet light with a wavelength of 365 nm. The concentration of the closed-ring isomer of the initial state was 10 mol %. Conversion efficiency from closed to open forms is related to the quantum yield of the photoisomerization reaction and the usual photoreaction quantum yield for DAE is 0.1 at a wavelength of 633 nm. The corresponding isomerization quantum yield for carrier injection, however, has not been defined due to the difficulty of estimating carriers on molecules. We, therefore, do not discuss about it here.

Figure 2(a) shows the EBL thickness dependence of the applied voltage-current characteristics. Injected current was decreased for thicker EBL devices, which was attributed to the lower electric field resulting from thicker total thickness and the blocking effect of electron injection. Both carriers, electron and hole, were able to be injected into the device with no EBL, but the electron injection was blocked for the thick EBL devices. In that case the hole-injection mechanism should have space-charge restriction because there are surplus holes in the organic layer. The current in the space-charge restriction mechanism is proportional to the square of voltage. To clear electron injection blocking effect, the voltage-current characteristics were replotted in Fig. 2(b) with the square voltage the horizontal axis and the vertical axis using normalized current by observed maximum current. Apparently, the current for thicker EBL devices approaches linear characteristics with square of voltage at the large current region, which means the holes are dominating the current.

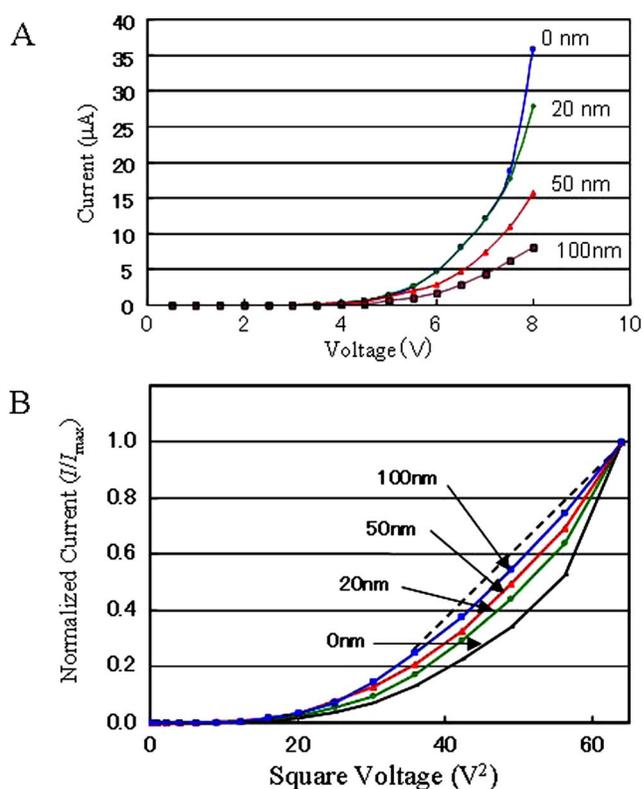


FIG. 2. (Color online) Voltage-current characteristics of the memory devices.

Isomerization speed by carrier injection, which was defined by the half decrease time of the current, was measured. Current decrease is caused by ionization potential change based on an isomerization reaction from a closed-ring to an open-ring state of DAE.¹³ Figure 3(a) shows the current decrease characteristics at constant voltage of 8 V for EBL devices of various thicknesses. The half decrease times of the current were 65, 45, 30, and 35 s for devices with EBL thicknesses of 0, 20, 50, and 100 nm, respectively. Half decrease time was shortened by increasing the EBL thickness even though the absolute current values became smaller, such as 35, 30, 18, and 13 μA for larger EBL thicknesses such as 0, 20, 50, and 100 nm, respectively. This result means that thicker EBL devices showed shorter recording time in spite of smaller injected current. To clear the isomerization reaction by hole injection into the closed-ring molecule, Fig. 3(b) was replotted using the vertical axis for normalized current and the horizontal axis for injected carriers defined by the product of current and time. This figure also indicates the isomerization efficiency of the injected carriers. The carriers for the half decrease of the 0 nm EBL device were 250 $\mu\text{A s}$, whereas the carriers for 50 and 100 nm EBL devices were both 50 $\mu\text{A s}$. This means that the 100 nm EBL device needs 20% carriers compared to the 0 nm EBL device for writing. The hole injection, therefore, reacts from the closed-ring molecules to the open-ring molecules with five times more efficiency than both carrier injections.

The corresponding quantum yield for hole isomerization cannot be defined because holes do not disappear, and they move in the ML and react with many molecules depending on the ML thickness. Hole-isomerization efficiency, however, depends on the lifetime of the cationic state of DAE molecules. Therefore, a longer lifetime of the cationic state,

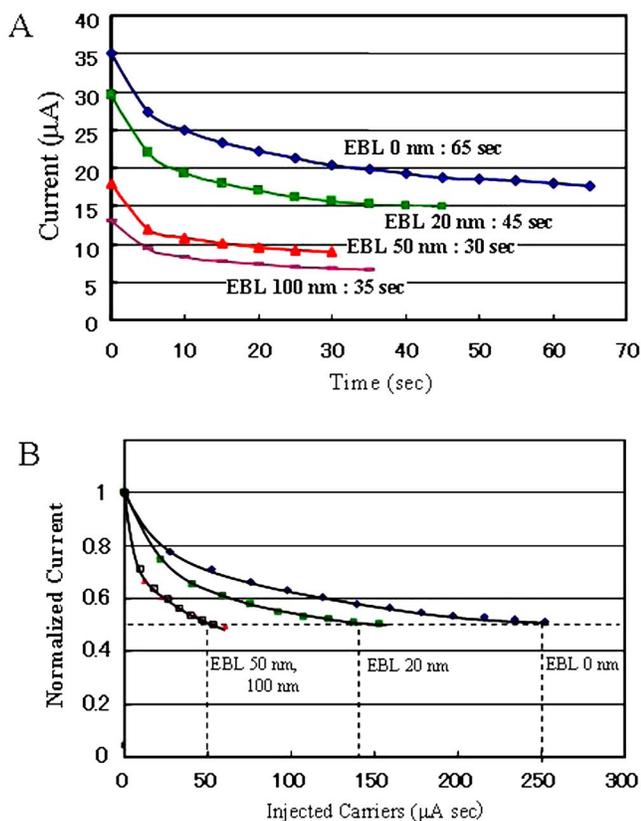


FIG. 3. (Color online) EBL thickness dependence of current decrease.

which originates from the low moving speed of the holes obtained by lowering voltage, would cause a large possibility of open-ring isomerization. To confirm this consideration, the applied voltage dependence of isomerization efficiency was measured for the 100 nm EBL device. Figure 4 shows the voltage dependence of the efficiency. The vertical axis is normalized by the initial current, and the horizontal axis is in the injected carriers. Efficiency was increased by lowering the voltage. The efficiency for a voltage of 6 V was 60 times of that for 10 V. This result also confirms efficient isomerization from a closed-ring to an open-ring state of DAE molecules in the film by hole injection.

In summary, the ring-opening isomerization reaction of DAE molecules in a solid film state by hole injection was studied by using the device with EBL. The high efficiency of isomerization, which originated from the long lifetime of the cationic state, was achieved by the hole injection with low voltage. Our demonstration presented here is important for

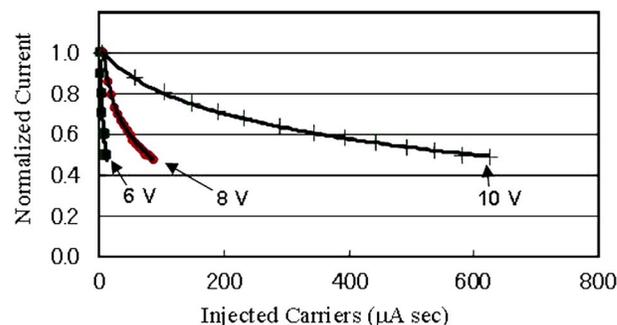


FIG. 4. (Color online) Applied voltage dependence of hole-isomerization efficiency.

realizing organic semiconductor memory with thermal stability and low power consumption. Hole-isomerization recording has the potential for very low power consumption organic memory.

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