Organic bistable molecular memory using photochromic diarylethene

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A principle of organic memory device using a bistable photochromic molecule is presented that allows extremely high bit densities and very low power consumption. This device is based on an isomerization reaction of photochromic diarylethene molecule via its excited state by an electric carrier injection, not by photon absorption. Experimental data show that the reversible writing and nondestructive reading of information by the carrier injection is feasible. The advantages and properties of such an organic semiconductor memory using a bistable molecule are discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1597966]

Electronic circuit chip and related semiconductor memory technology have been marching in step for decades. But the ability to cram ever more circuitry onto silicon chips now faces fundamental limits. Ironically, it is now possible to make the innards of a circuit, the transistors, resistors, capacitors, and wires, so small they no longer function. Since Ratner and Aviram suggested building computers from the bottom up by turning individual molecules into circuit components in 1974,[1] scientists have tried to get around these limits by going for the ultimate in shrinkage: turning single molecules and small chemical groups into transistors and other standard components of electronics circuit chips, and wiring them to a circuit.[2] Many kinds of molecular devices and their working principles, such as the molecular diode,[3] the molecular fuse,[4] and the molecular switch or transistor,[5,6] have been proposed as the most basic and essential elements in the electronics chip designer's tool kit.

Molecular switches function as molecular memory devices have been proposed,[7,8] but only under specific stimuli or conditions, such as under an electric field or at very low temperature. The molecular memory devices proposed, therefore, are completely unstable and can not keep a stored information bit at room temperature for a long time.

Here we present a principle for an organic molecular memory device that would be used to construct a nonvolatile, ultrahigh density, and extremely low power consumption memory device. Such a memory device is based on a reversible isomerization reaction of a photochromic bistable molecule by an electric carrier injection. This is achieved by a carrier (hole and electron) encounter excitation of the molecule of a diarylethene derivative.

Photochromic diarylethene derivatives with heterocyclic rings are well known to have the characteristics of good thermal stability, high fatigue resistance and rapid response.[9,10] Its open-ring form absorbs a photon in the ultraviolet region of the optical spectrum, and on the excitation yields closed-ring form with a different spectrum. This closed-ring form absorbs in the green-red region of the visible spectrum and returns into the open-ring form. The diarylethene derivatives are expected as a photoreactive molecule for obtaining an ultrahigh density photon-mode optical memory.[10,11]

We emphasize that this method is based on the electric carrier injection and the excitation via the encounter of the bistable molecule of a hole injected from the anode and an electron injected from the cathode (named electron-mode recording), not on the photoexcitation (photon-mode recording). The electron on lowest unoccupied molecular orbital level and the hole on highest occupied molecular orbital level of the molecule produce the excited state identical to that produced by photoexcitation, so the molecule is transformed into another isomerization form. For the case of diarylethene derivatives, the ionization potential I_p of the molecule is changed according to its isomerization form. The closed-ring form (colored form) has I_p of 5.7 eV and the open-ring form (uncolored form) has above 6.2 eV.[12,13] The information readout is achieved by detecting the electric current through the molecule affected by the difference of I_p.

The advantages of such a organic bistable molecule memory are (i) immense information storage capacity (ultimately, 1 bit/molecule), (ii) random access, (iii) very low power consumption for writing (ultimately, 1 bit by a single pear of a electron and a hole), and (iv) conventional semiconductor manufacturing process is applicable (for an organic and inorganic hybrid semiconductor memory system as mentioned later).

The information storage process involves writing, reading, and erasing in a binary format provided by the two distinct molecular forms of the diarylethene. In order to explain the principle of the memory, we adopted the cell structure with organic multi layers, like that of organic light emitting devices. Energy level diagrams of the ''writing'' and ''reading'' processes are displayed in schemes 1 and 2 in Fig. 1, respectively. For writing, electrons injected from the cathode and holes from the anode with relatively high voltage are transported to the bistable molecule layer via carrier transport layers, and they excite the bistable molecule in the closed-ring state, and then the molecule is transformed into the open-ring state and its ionization potential becomes large (scheme 1). For reading, only the holes or electrons flow in the organic layers because of the relatively low applied voltage and the unbalanced potential barrier heights between electrodes and organic layers. Charge stream occurs but the molecules are not excited, so the nondestructive readout is achieved by detecting the current. The magnitude of the cur-

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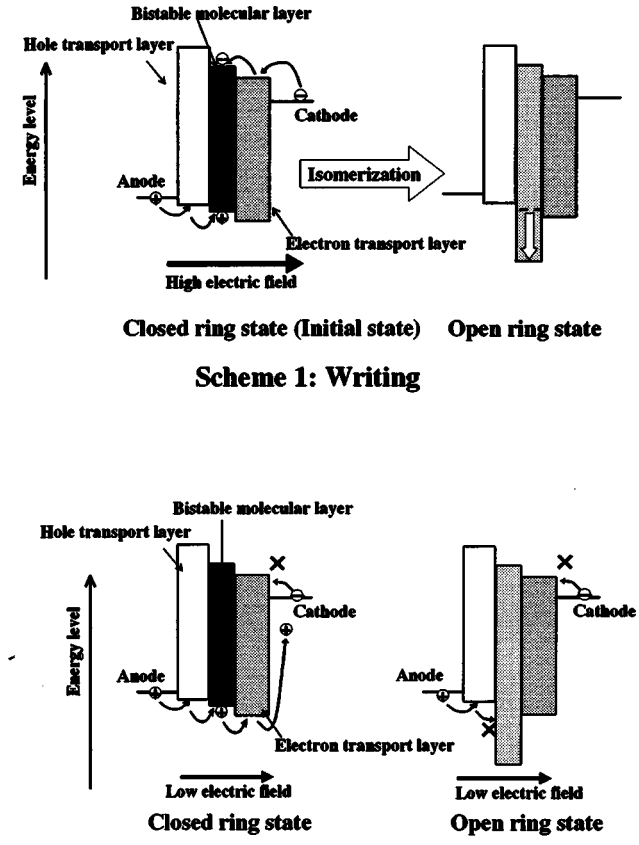

FIG. 1. (a) Principle of the electron-mode writing scheme. (b) Principle of the nondestructive readout. The vertical and horizontal axes indicate the energy level and the direction of device thickness, respectively.

rent is varied with the isomerization state of bistable molecule layer (scheme 2). Erasing may be achieved by irradiating light with an ultraviolet wavelength.

In order to obtain such a memory device, a bipolar diarylethene derivative is required. The diarylethene having hole transport characteristics can be obtained by modifying the aryle rings with a triphenylamine group.[13] We, therefore, designed a nonsymmetrical bipolar diarylethene with a triphenylamine group and an oxadiazole group, which exhibited electron donor and acceptor characteristics, respectively, as shown in Fig. 2.

The thin film sample was used in the experiment to confirm the writing and reading principles. The sample cell of the memory was prepared on indium tin oxide (ITO) (anode) glass substrate by vacuum evaporation method. The organic layers and the cathode layer were deposited. The cell structure was as follows: ITO/hole injection layer [4,4′,4″-tris[*N*-(1-naphthyl)-*N*-phenyl-amino]-triphenylamine 35 nm]/hole transport layer [*N*,*N*′-di(naphthalene-1-yl)-*N*,*N*′-diphenyl-benzidine 25 nm]/bistable molecule layer (bipolar diarylethene, 25 nm)/cathode layer ($Mg_{0.9}In_{0.1}$).

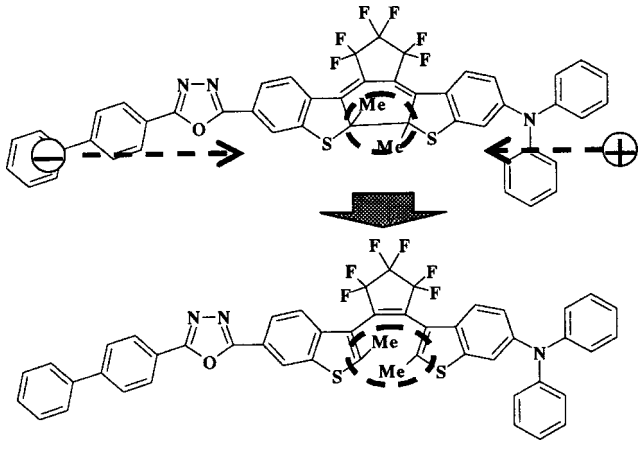

FIG. 2. Molecular structure of bipolar diarylethene derivative used in the experiment.

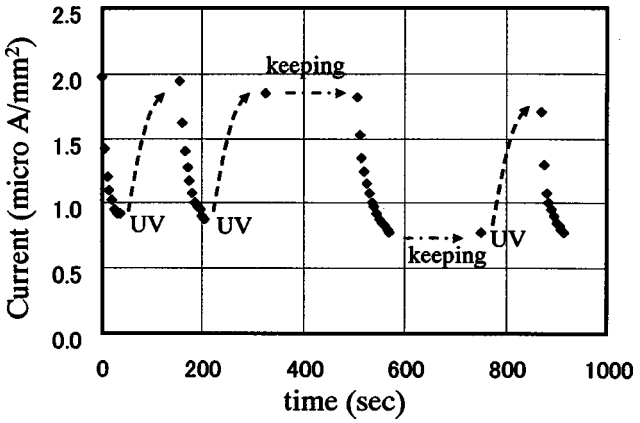

FIG. 3. Experimental data of reversible writing. The applied voltage was kept at 2 V (constant voltage operation). The sample was left without any voltages under the dark environment at room temperature for the time displayed as keeping.

Figure 3 shows the experimental data of reversible writing scheme 1. The constant voltage of 2 V was applied to the sample in the initial colored state (conversion ratio to closed-ring form was 10 mol %) generated by the ultraviolet light irradiation, and the change of current was observed. The current for the initial state was 2.0 μA/mm^2, but the current decreased to 0.8 μA/mm^2 by the carrier injection. The current decreasing is attributed to the isomerization reaction of the bistable diarylethene molecule by the electron-mode reaction. The decreased current state corresponds to the recorded state and was recovered to the initial (erased) state by irradiating the ultraviolet light. The change of current indicates that the information readout can be carried out by detecting the current corresponding to the isomerization state. Both of the bit stored state and the initial state were stable under the dark environment at room temperature (displayed as ''keeping'' in Fig. 3). Therefore, the principle of electron-mode recording of the bistable molecular memory was demonstrated.

Nonlinear isomerization reactivity with injected current magnitude was also observed. Figure 4 shows the initial current magnitude dependence of the time required for writing. Lines 1 and 2 were the data of initial current $I_1 = 1.85$ μA/mm^2 (voltage 2.0 V) and $I_2 = 0.88$ μA/mm^2 (1.7 V), respectively. The vertical line was normalized by each initial injected current. Even though the initial current with a half magnitude was injected ($I_2 = I_1/2$), the time for a half decrease of the current was not twice but about four times. This nonlinearity is attributed to the unbalanced carriers described in scheme 2 and, therefore, nondestructive readout would be achieved by using a small current.

The data presented here show the feasibility of the ultra-

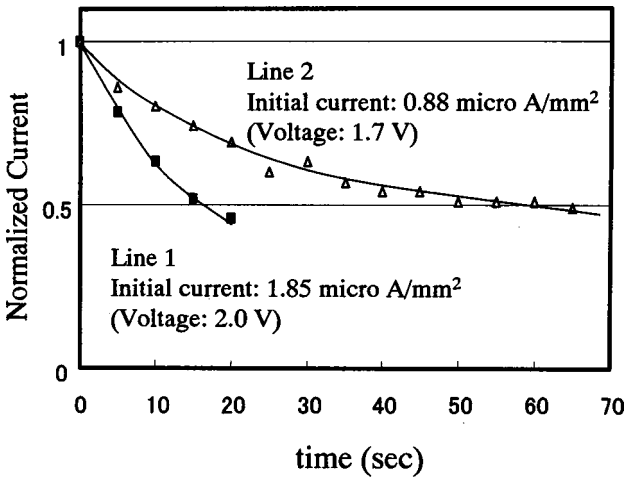

FIG. 4. Nonlinear isomerization reactivity with injected current magnitude. Conditions 1 and 2 were the data of initial current $I_1 = 1.85\ \mu A/mm^2$ (applied voltage 2.0 V) and $I_2 = 0.88\ \mu A/mm^2$ (1.7 V), respectively. The vertical line was normalized by each initial injected current.

high density molecular memory device based on carrier injection excitation isomerization of the bistable molecule. An obvious advantage of this memory, in addition to the molecular scale storage density, is to have ultralow power consumption and very fast speed for writing. No power is required to keep storage data because of the thermal stability of the isomerization forms of the diarylethene molecule, and it has the feasibility of extremely low power to write a bit on the bistable molecule. Only one carrier pear (hole and electron), that is, a single electron through the molecule, corresponds to the isomerization reaction of the molecule in principle. So this memory device would be a stable single electron molecular memory device if carrier balance is optimized and a high sensitive molecule with the isomerization quantum yield of 1[10] is adopted.

Furthermore, this memory principle can be applied to solve a problem for a conventional inorganic semiconductor memory device, such as a dynamic random access memory (DRAM) or a flash electrically erasable programable read only memory (flash EEPROM). In conventional semiconductor technology, the minimum design rule with less than 0.1 μm has been achieved and a 10 nm order rule will be practical in the near future. There is, however, a well-known problem in semiconductor memory devices in obtaining an ultrahigh integrated semiconductor memory. The conventional memory cell has a switching (transistor) element and a storage element. It is hard to reduce the storage element in a memory cell because of the problems of current leaks at a floating gate in flash EEPROM or of a three-dimensional capacitor in DRAM. As shown in Fig. 5, the cell of an organic and inorganic hybrid memory, which has a conventional Si-based switching element and the bistable molecular storage element, can be easily reduced because the storage

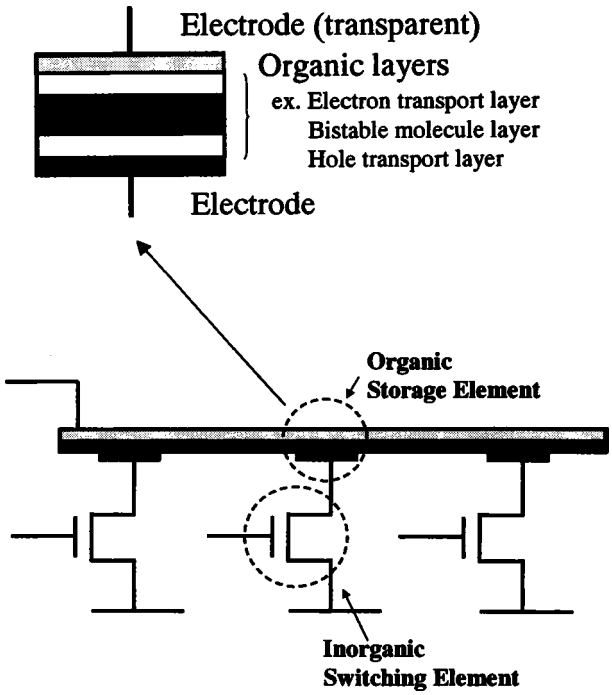

FIG. 5. Concept of the hybrid memory cell. The cell consists of a switching element of conventional inorganic Si transistor and a storage element of the organic bistable molecules.

element can have the very small area of bistable molecules. Also, only a minor change of the process would be required for producing such a hybrid memory, since the cell would be feasible simply by depositing the unpatterned uniform organic layers and the electrode layer on the usual Si substrate with integrated circuit patterns fabricated by using the conventional process technology.

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