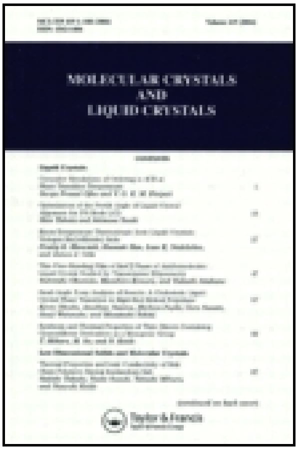

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Electrical Molecular Memory Using Diarylethene Derivatives

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Electrical Molecular Memory Using Diarylethene Derivatives

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This paper presents a principle for a novel electrical molecular memory device using a photochromic diarylethene, which has the potential ability of inexpensive, disposable, extremely high bit-density, and very low power consumption. This device is based on an isomerization reaction of the diarylethene molecule via its excited state by injection of electric carriers, not by photon absorption. The reversible writing by carrier injection is demonstrated. The advantages and applications of the molecular memory are discussed.

Keywords: diarylethene; electric carrier injection; molecular memory; organic semiconductor; photochromism

INTRODUCTION

Development of both electronic circuit chips and related semiconductor memory technology has been marching in step for decades. However, 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 that they can no longer function. Scientists have tried to circumvent these limits by attempting the ultimate in shrinkage. Their efforts have yielded many working principles and proposals for different types of molecular devices that form the basic and essential elements of these chips [1–4]. The electrical molecular memory devices proposed, however, are unstable and cannot retain stored information at room temperature for a long time. In this paper, we propose a novel principle for an electrical molecular memory device that would be used

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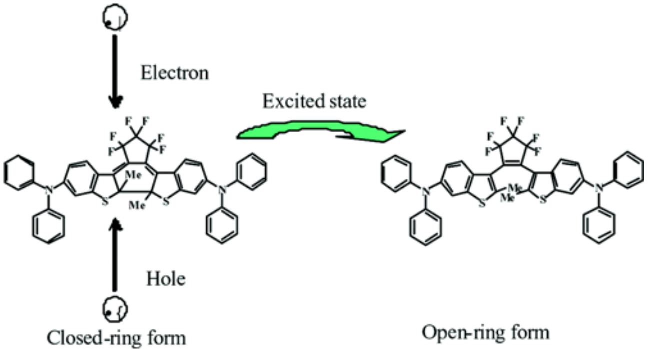

FIGURE 1 Isomerization reaction of the diarylethene derivative by electrical carrier injection.

to construct a memory device with ultra-high density and extremely low power consumption.

ISOMERIZATION REACTION BY ELECTRICAL CARRIER INJECTION

This memory is based on electric carrier injection into diarylethene molecules [5,6] and excitation via the encounter on the molecule of a hole and an electron, not on the photo excitation, as shown in Fig. 1. The electron at the LUMO (Lowest Unoccupied Molecular Orbital) level and the hole at the HOMO (Highest Occupied Molecular Orbital) level of the molecule produce the excited state, thereby transforming the molecule to another isomerization form [7]. The ionization potential (I_p) of the molecule changes according to its isomerization form: the closed-ring form (colored form) has an I_p of 5.7 eV, while the open-ring form (uncolored form) has a value above 6.2 eV.

The information storage process involves writing, reading, and erasing in a binary format provided by the two distinct molecular forms of the diarylethene. Usually, the memory device has a multi-layered structure. Energy level diagrams of the “writing” and “reading” processes are displayed in Schemes 1 and 2 in Fig. 2, respectively. In the “writing scheme,” 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. They excite the diarylethene molecule in the closed-ring state, and then the molecule transforms to the open-ring state with a large ionization potential (Scheme 1). For the “reading scheme,” only the holes

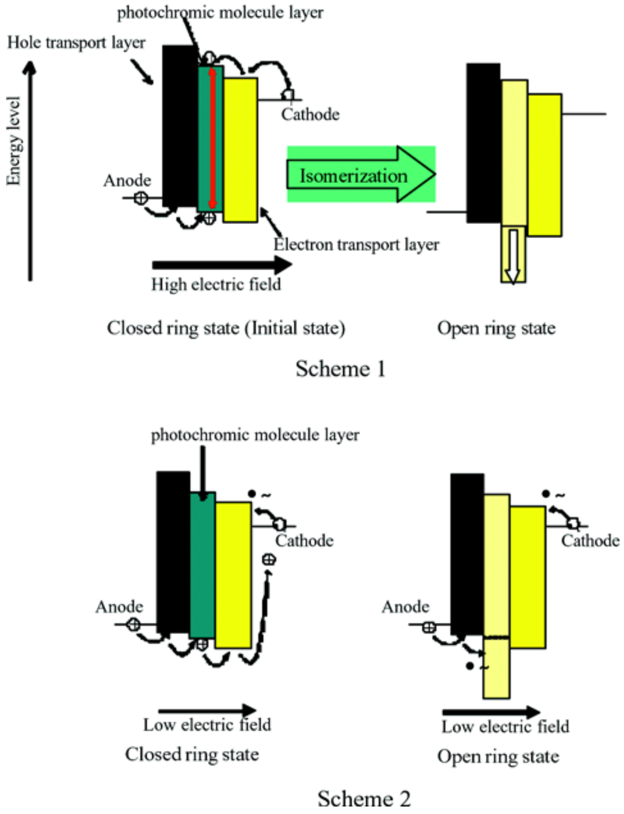

FIGURE 2 Writing and reading schemes.

flow in the organic layers due to the relatively low applied voltage and the unbalanced potential barrier heights between electrodes and organic layers. Because the charge stream occurs but the molecules remain unexcited, the readout is achieved by detecting the current without affecting the stored information. The magnitude of the current varies according to the stored information, that is, the isomerization state of the molecules (Scheme 2). Erasure is achieved by irradiating the molecules with ultraviolet light.

EXPERIMENTAL

An experimental memory cell was prepared on an indium tin oxide (ITO, anode) glass substrate by the vacuum evaporation method.

The organic layers and the cathode layer were deposited on the substrate in turn. The cell structure was as follows: ITO/hole injection layer (4,4′,4″-Tris(N-(1-naphthyl)-N-phenyl-amino)-triphenylamine, 2TNATA, 20 nm)/hole transport layer (N,N'-di(naphthalene-1-yl)-N,N′-diphenyl -benzidine, α-NPB, 30 nm)/memory layer (diarylethene, 20 nm)/cathode layer ($Mg_{0.9}In_{0.1}$). In some cases, an electron transport layer was added between the memory layer and cathode. The area of the cell was 4 mm^2.

Figure 3 shows the photo-reversible "writing" according to Scheme 1. A constant voltage of 6 V was applied to the sample in the initial colored state generated by ultraviolet light irradiation, and a change of current was observed. The current for the initial state was 8 μA, but the current decreased to 3 μA following electrical carrier injection. The reduced current state corresponds to the recorded state. The cell recovered to the initial (erased) state by irradiation with ultraviolet light. This decrease in the current was attributed to the isomerization reaction of the diarylethene molecule. The change in the current indicates that it is possible to read information by detecting the current. Both the bit-stored state and the initial state were stable under the dark environment at room temperature (displayed as "Under dark" in Fig. 3). These results demonstrated the writing principle of the electrical molecular memory.

Nonlinear isomerization reactivity with injected current magnitude was observed. Even though the initial current with a half magnitude was injected, the time for a half decrease of the current was not twice but about 4 times. This nonlinearity is attributed to the unbalanced carriers described in Scheme 2 and, therefore, there is the potential to achieve the readout without destroying stored information is achieved by using a small current.

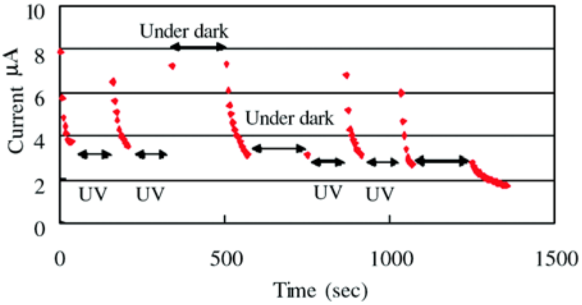

FIGURE 3 Photo reversible "writing".

ADVANTAGES AND APPLICATIONS

The memory principle presented here would be applied to the various memory devices. Advantages of this memory are to have the potentials for the molecular-scale storage density and ultra-low power consumption. It has the potential of extremely low power to write a bit. Because only a single carrier pair (hole and electron), that is, a single electron through the molecule, corresponds to the isomerization reaction of the molecule in principle, this memory device would be a stable single-electron molecular memory device by optimizing the carrier balance and adopting a highly sensitive molecule with the isomerization quantum yield. This indicates the feasibility of future single-molecular memory devices.

Furthermore, this memory principle can be applied to solve other problems of conventional semiconductor memories, such as dynamic random access memory (DRAM) or flash electrically erasable programmable read-only memory (flash EEPROM). There is the well-known problem in semiconductor memory devices of obtaining an ultra-high integrated semiconductor memory. The conventional memory cell has a switching (transistor) element and a storage element. It is difficult 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. The cell size of an organic and inorganic hybrid memory, which has a conventional Si-based switching element and a molecular storage element, however, can be easily reduced because the storage element can have the very small area of several molecules.

One important application of this memory is as a very cheap and disposable memory that could be used in RFID tags. A combination of this memory, an organic thin film transistor and printable circuit technology should permit the production of such a cheap and disposable organic device in the near future.

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