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In-plane electrical bistability of photochromic diarylethene/Cu composite film

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ABSTRACT

Electrical bistability is an essential property for memory devices. We report here the in-plane electrical bistability of photochromic diarylethene (DAE)/Cu composite film, which is prepared by Cu vapor deposition on the DAE surface with a low glass-transition temperature. The low-current level around 10^{-8} A was switched to a high-current level of ca. 10^{-4} A at a low threshold voltage (V_{th}) in the first voltage sweep. Once this switching occurred, the high-current level was kept in the second voltage sweep, and electrical bistability was achieved for the in-plane current. V_{th} was distributed in a wide range of voltages (0.5–10 V), and the colored sample obtained by the UV irradiation showed a relatively higher V_{th} than the colorless sample. The highest ON–OFF ratio in current was ca. 10^6. The origin of the bistability attributed to the electrical breakdown in the insulated lines that was consisted of DAE in Cu film. The in-plane bistability of the DAE/Cu composite film has good retention time (>60 min) and readout-cycle endurance (>10^6 cycles), indicating that it is suitable for write-once organic semiconductor memory characteristics.

1. Introduction

Electrical bistability is an essential property for obtaining organic semiconductor memory devices. Many kinds of memory devices with bistability have been reported so far [1–3]. The mechanisms of bistability for some of them are based on a molecular conformation change [4], the isomerization of photochromic molecules [5–9], a filamentary conduction mechanism [10], or carrier traps on conductive nanoparticles [11–19]. All of these devices have a structure with an organic (or organic/metal composite) layer or organic layers sandwiched by two electrodes, and electrical carriers are conducted in the direction of the film thickness (vertical) between the electrodes. Electrical bistability occurs perpendicularly to the organic layer, and the devices have characteristics of low operating voltages because of the short distance between the two electrodes.

We found an analogous but in-plane electrical bistability with a low operating voltage for a photochromic diarylethene(DAE)/Cu composite film, which was prepared by vacuum evaporation of Cu onto low glass-transition temperature (low-Tg) DAE film. Photochromic materials show a reversible change in molecular structure by light irradiation; various properties also change reversibly, including absorption, Tg, conductivity, and/or electrical permittivity [20,21]. In this paper, we report the origin, the characteristics, and the potential of memory devices for the in-plane electrical bistability of DAE/Cu composite film.

2. Experimental and results

Fig. 1(a) shows the photochromism of a DAE molecule used in our experiment. The colorless molecule (open-ring state) reacts into the colored molecule (closed-ring state) upon UV light irradiation and reverts to a colorless molecule upon visible light irradiation. We prepared a Cu/DAE composite film showing electrical bistability by the following process (Fig. 1(b)). A colorless amorphous DAE layer was prepared on a glass substrate by conventional vacuum evaporation (deposition rate: 1–5 nm/s, thickness: 30 nm, base pressure: 1×10^{-5} Torr). Then Cu was deposited on the colorless DAE layer using a vacuum evaporation method at a substrate temperature of 50 °C and a deposition rate of 0.075 nm/s, where the condition of the 10-nm-thick of deposited Cu film corresponded to that on a glass substrate. The Cu film on the DAE surface consisted of Cu nanocrystals [22]. Then the film was exposed to an O_3 atmosphere for 20 min to oxidize the surface of the Cu nanocrystals. (The film that was not oxidized did not show bistability.) We measured the in-plane current–voltage (*I–V*) characteristics of the DAE/Cu composite film using tungsten micro-probes at a distance of 0.5 mm (Fig. 1(c)).

Fig. 2(a) shows the electrical bistability of the colorless (left figure) and colored (right figure) Cu-DAE composite films. The *I–V* characteristics for the colorless and colored samples, which were

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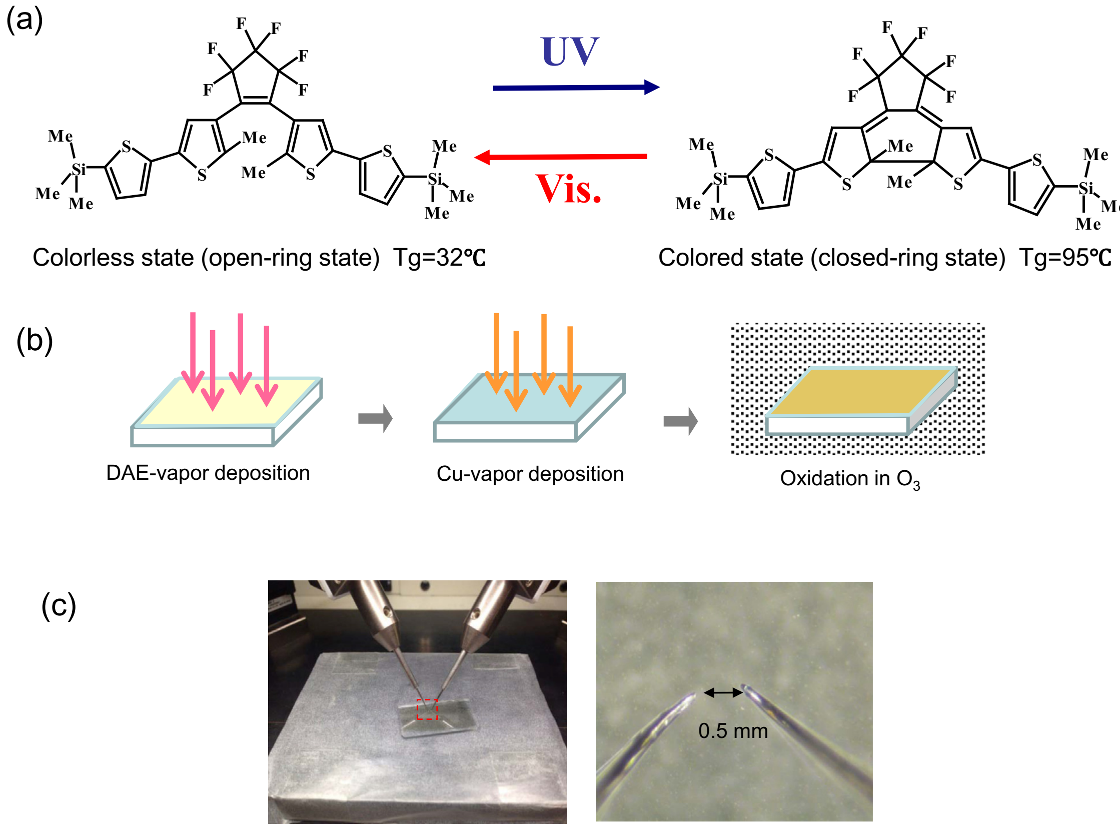

Fig. 1. (a) Photochromism of DAE; (b) preparation process of DAE/Cu composite film; (c) measurement of in-plane *I*–*V* characteristics using a micro-prober system.

just after the O_3-process in Fig. 1(b) and after sufficient UV irradiation (λ = 365 nm) of the colorless sample, respectively, were measured. The current of the colorless sample was gradually increased at a low level from 10^{-10} to 10^{-8} A with the first voltage sweep from 0 to 4 V and a sudden jump to a high level of 10^{-4} A was observed at a threshold voltage (V_{th}) of 4 V. On the other hand, the colored sample shows analogous *I*–*V* characteristics and a higher V_{th} (ca. 9 V). In both cases, after switching to a high-current level was achieved, the second voltage sweep generated a high-current level; write-once electrical current bistability was observed. Sheet resistance of the film in high-current state was ca. 1 Ω/sq.

The V_{th}, however, were distributed in a considerably wide range. Fig. 2(b) shows the distribution of the V_{th}s for the colorless and colored samples. The colored samples show relatively higher V_{th}s than the colorless samples. The count values at 0 V mean that the samples show a high-current level even at 0 V, and no threshold was observed. Those at $15 < V$ in Fig. 2(b) mean that the samples showed a low-current level in a range of 0–15 and no threshold.

Fig. 2(c) shows the overlaid *I*–*V* characteristics of the colorless and colored samples with various V_{th}s. In addition to V_{th}, these have the same high- and low-current levels, indicating that a lower V_{th} corresponds to a higher ON–OFF ratio. The highest ON–OFF ratio was ca. 10^6 at the V_{th} of 0.5 V.

3. Origin of the bistability

To study the origin and mechanism of electrical bistability, first we investigated the Cu-thickness dependence. The top figure in Fig. 3(a) shows the *I*–*V* characteristics of the colorless samples. When the thickness was 10 nm, bistability was observed. When the thickness was 15 or 5 nm, however, the current level was high or low, respectively, and no bistability was observed.

We also measured the *I*–*V* characteristics of the pre-colored samples, which were reference samples prepared by Cu-evaporation onto the colored DAE layer. All pre-colored samples showed no bistability (bottom figure in Fig. 3(a)). A Cu film deposited on a glass substrate as a reference sample showed no bistability. This result indicates that Cu-evaporation onto the colorless DAE layer is essential to obtain bistability.

Atomic-force microscope (AFM) images were recorded on the colorless and pre-colored samples after Cu evaporation (Fig. 3(b)). Many Cu nanocrystals with a diameter of several tens of nm were observed on the 5-nm-thick colorless sample, but the larger and connected crystals were observed for the thicker Cu colorless samples. On the other hand, no significant changes were observed on the Cu nanocrystals on the pre-colored samples; high density and many Cu nanocrystals with a 10–20 nm diameter were observed for all the precolored samples. The crystal size is depending on activity of surface atom diffusion; less-active atom diffusion leads many crystal nucleation and small crystal growth. Pre-colored surface with high-Tg causes less-active surface molecular motion, and therefore causes small crystal [23]. This result suggests that large and connected Cu-crystal structure is important to achieve electrical bistability.

To understand the current mechanisms, we replotted the *I*–*V* characteristics. The left and right figures in Fig. 4(a) show the replots of the low- and high-current levels in the left figure (colorless sample) in Fig. 2(a). The data of the low-current level were plotted by the square root of the voltage in the horizontal axis and by log *I* in the vertical axis. The straight line in the graph means that the current obeys a thermal emission mechanism such as the Schottky mechanism. On the other hand, the replot of the high-current level indicates ohmic conductance. The same