Surface-type nonvolatile electric memory elements based on organic-on-organic CuPc-H_2Pc heterojunction*

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A novel surface-type nonvolatile electric memory elements based on organic semiconductors CuPc and H_2Pc are fabricated by vacuum deposition of the CuPc and H_2Pc films on preliminary deposited metallic (Ag and Cu) electrodes. The gap between Ag and Cu electrodes is 30–40 μm. For the current–voltage (I–V) characteristics the memory effect, switching effect, and negative differential resistance regions are observed. The switching mechanism is attributed to the electric-field-induced charge transfer. As a result the device switches from a low to a high-conductivity state and then back to a low conductivity state if the opposite polarity voltage is applied. The ratio of resistance at the high resistance state to that at the low resistance state is equal to 120–150. Under the switching condition, the electric current increases ∼ 80–100 times. A comparison between the forward and reverse I–V characteristics shows the presence of rectifying behavior.

Keywords: heterojunction nonvolatile memory, organic-on-organic, CuPc, H_2Pc

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1. Introduction

Recently, a lot of work has been done in the field of organic based electronic devices. These materials provide a diversity of interesting properties, which make possible the realization of organic electronic devices with advantages over the conventional inorganic technology.[1–3] The motivations in using organic materials in electronic devices come from their ease in tuning electronic and processing properties by chemical design and synthesis, low cost and low temperature processing, reel-to-reel printing, mechanical flexibility, and compatibility with flexible substrates. Flexible electronic displays, circuits, sensors and memories will enable the future generation of electronics based on organic active materials.[4]

Non-volatile memory (NVM) devices based on conventional silicon technology have experienced the development process in applications from computer to portable flash drives. During the past few years, research work in the area of memory devices based organic and inorganic semiconductors, nanocomposites and polymer materials has been developed well.[5,6] Electrically bistable devices based on organic materials show a non-volatile memory effect.[7] The electric-field-induced charge transfer from an organic electron donor to an acceptor is considered as a responsible mechanism for the memory effect which switches the device from a low- to a high-conductivity state. In the review,[8] the switching behavior and the nonvolatile memory effect have been presented by investigating the I–V characteristics in many organic semiconductor devices based on polymer and low molecular materials. In the review,[9] the information about nonvolatile memory devices based on hybrid inorganic/organic nanocomposites has been presented. In particular, the structures, fabrications, electrical characteristics, switching and carrier transport mechanisms of nonvolatile memory devices were discussed. For a large area of low-cost electronics, there is a need to develop alternate cost-effective memory devices. The emerging field of organic electronics has potential for low cost nonvolatile memory applications due to its key advantages of simple and low-temperature thin-film processing through inexpensive techniques such as spin coating, ink-jet printing, or stamping.[10]

The memory device based on polypyrrole (PPy) nanoparticles embedded in poly (vinyl alcohol) (PVA) was fabricated and investigated by Hong *et al.*[11] They found that with a 20-nm-thick PPy layer in the memory devices, the stable multilevel switching takes place with a high on/off ratio that was over 100. A memory element based on poly-epoxypropylcarbazole (PEPC) and tetracyanoquinodimethane (TCNQ) has been reported by Akhmedov *et al.*[12] On the Cu substrate, there was deposited a film of the PEPC–TCNQ complex followed by the deposition of aquadag film that played the role of the counter electrode. In the I–V

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characteristics, the switching and nonvolatile memory effects were observed. At switching, the resistance of the samples is decreased 100 times. The high resistance state of the memory element was restored by heating at 55–60 °C. Copper phthalocyanine (CuPc) is a well-known organic semiconductor that has been investigated for the many electronic devices.[13] In Ref. [14], the memory element Al/Alq_3/CuPc/Alq_3/Al was investigated, where Alq_3 is aluminum tris (8-hydroxyquinolate) which is a well investigated organic semiconductor.[13,15] An overview of emerging nonvolatile memory technologies was presented in Ref. [16]. This review focuses on electrically programmable nonvolatile memory changes from silicon nanocrystal memory scaling to organic semiconductors. Metallic nanoparticles based memory devices and emerging nonvolatile memory devices fabricated by the use of flexible and transparent redox-based resistive switching memory technologies have been discussed. In that review, an overview is presented of storage systems and components from conventional memory devices to the devices based on nanostructured materials as a redox-based resistive random-access memory (RRAM) and three-dimensional (3D) transparent memory devices. An advancement in organic nonvolatile memory devices has been further described in Ref. [17]. In particular, two structures of memory devices were described, i.e., two-terminal (resistive devices), and three-terminal (transistor) devices. Owing to the reliability of operation and simplicity at fabrication the two-terminal memory devices are very popular.

Therefore, in the present study, we used CuPc and metal free phthalocyanine (H_2Pc) to fabricate two terminals, resistive memory devices, CuPc and H_2Pc have different work functions, 3.87 eV and 4.04 eV, respectively. This difference in work functions potentially allows one to fabricate a donor–acceptor system. The energy gaps of the CuPc and H_2Pc are equal to 1.6 eV[18,19] and 2.2 eV, respectively, that can allow one to fabricate a heterojunction. Usually, the memory devices are sandwich-type that have a number of advantages as lower resistance and higher currents. At the same time, practically, it is difficult to avoid the short-circuiting of the devices during the fabrication process, especially if the thickness of the semiconductor films is small. Therefore, it seems, surface-type devices are more reliable, where there is a gap between two metallic films that can be filled with semiconductor materials with appropriate technology. Thus, it would be reasonable to fabricate and investigate the surface type memory element. The materials used in the study are the organic semiconductors known as CuPc and H_2Pc.

2. Experiment

For the fabrication of surface-type memory elements, commercially available CuPc and H_2Pc were purchased from Sigma Aldrich. CuPc and H_2Pc have chemical formula $C_{32}H_{16}CuN_8$ and $C_{32}H_{18}N_8$, respectively. Molecular structures of the CuPc and H_2Pc are shown in Fig. 1(a). The CuPc is a p-type organic semiconductor.[13,18] CuPc exists in seven crystalline polymorph states: $\alpha, \beta, \gamma, R, \delta, \varepsilon$, etc.[19] The α-CuPc form is metastable at 165 °C and can be converted thermally into β-form. The α and β forms are the most frequently encountered states of CuPc. The fabricated CuPc films were in β-form because thermal sublimation was used for film deposition. The structure that characterizes the β-form is a monoclinic crystal P_{21}/a with $a = 19.407$ Å, $b = 4.79$ Å, $c = 14.628$ Å, and $\beta = 120.93$ Å.[19] It has a conductivity of 5×10^{-13} Ω^{-1} cm^{-1} at $T = 300$ K.[20,21] The molecular weight of the CuPc molecule is 576 amu. Its sublimation temperatures vary from 400–580 °C at a pressure of 10^{-4} Pa.[22] Figure 2 shows the schematic diagrams of the nonvolatile electric memory surface-type elements based on organic semiconductors CuPc and H_2Pc. The gap between Ag and Cu electrodes was between 30–40 μm for different samples.

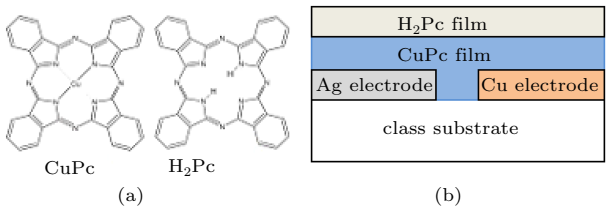


Fig. 1. (color online) (a) Molecular structures of the CuPc and H_2Pc. (b) Schematic diagram of the nonvolatile electric memory surface-type element based on organic semiconductors CuPc and H_2Pc.

To fabricate the elements (Fig. 1(b)) on glass substrate, first, the silver and copper films were deposited by vacuum evaporation. Over the metallic films, CuPc and H_2Pc were deposited consequently. Metals and organic semiconductors were deposited by using an EDWARD 306 vacuum thermal evaporator. The rates of deposition of copper, silver, CuPc and H_2Pc were 0.05 nm/s, 0.04 nm/s, 0.24 nm/s, and 0.14 nm/s, respectively. The length and width of the substrates were 16 mm and 14 mm, respectively. The gap between Ag and Cu films was 30–40 μm. The sublimation temperature of organic semiconductors was 460 °C, whereas the vacuum chamber pressure was 10^{-4} Pa. Thickness values of Ag and Cu films were both equal to 100 nm. Positive (+) potential in forward bias was applied to "Cu" film. To confirm the repeatability of the results, testing of samples was carried out 10–12 times. Atomic force microscopy (AFM) has been used to examine the surface morphologies of the CuPc and H_2Pc films. The AFM topographic images are shown in Fig. 2. The difference in surface topography between the two films is clearly observed in the figures. The morphologies of the stand-alone CuPc and H_2Pc films exhibit rough and non-uniform distinct features.

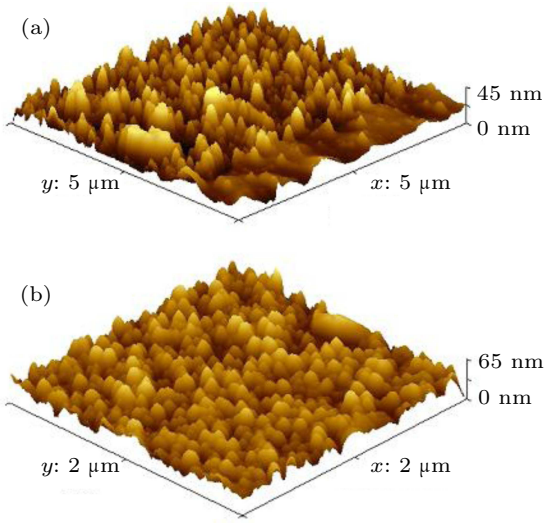


Fig. 2. (color online) The 3D AFM images of the CuPc (a) and H_2Pc (b).

3. Results and discussion

Figures 3(a) and 3(b) show the *I–V* characteristics of the two memory elements, where gaps between Cu and Ag metallic electrodes are 30 μm and 40 μm, respectively. In both cases, nonvolatile memory effect, switching effect, and negative differential resistance (NDR) are all observed. It is found that if the gap between metallic electrodes increases, the threshold voltage value (V_{Th}) also increases. In the forward bias condition, V_{Th} values are equal to 1.3 V and 1.5 V for the devices with 30-μm and 40-μm gaps, respectively. As the work functions of metallic films Cu and Ag are different (Cu has 4.65 eV and Ag has 4.26 eV), there exists an asymmetric behavior in the *I–V* characteristic. In fact, in the memory element there are two conductive channels for the charges' motion (see Fig. 1(b)), i.e., Ag–CuPc–Cu and Ag–CuPc–H_2Pc–CuPc–Cu. It can be assumed that in the forward current direction, the total resistance of the sample is lower than the total resistance in the opposite direction. This model can explain the experimental *I–V* characteristics up to some extent (see Figs. 3(a) and 3(b)). Regarding the working mechanisms of the nonvolatile memories, there are several approaches. In Ref. [7], the switching mechanism is explained by electric-field-induced charge transfer of electrons from a donor to an acceptor. In this process, the memory element is switched from a low to a high conductivity state. Another mechanism that was discussed in the literature is the formation of the highly conductive pathways in the composite layer.[9] The mobile metallic ions from the electrodes can migrate through a conductive filament between the two electrodes, when high enough voltages are applied to the device. It has been observed by using a current-sensing atomic force microscope. As the filament is metallic in nature, the temperature dependence of the current is very low. In Simmons and Verderder's model,[1] when the traps are occupied by charges, the device is in the high resistive state, and if the traps are empty, the device is in the low resistive state. The trapped charge can be removed by applying larger voltage biasing to the device. Therefore, the switching effect that is due to the trapping-detrapping mechanism can be observed. Concerning the nonvolatile memory effect observed in CuPc–H_2Pc elements, it can be assumed that the switching mechanism is due to the electric-field-induced charge transfer of electrons from a donor to an acceptor. In this process, the memory element switches from a low to a high conductivity state.

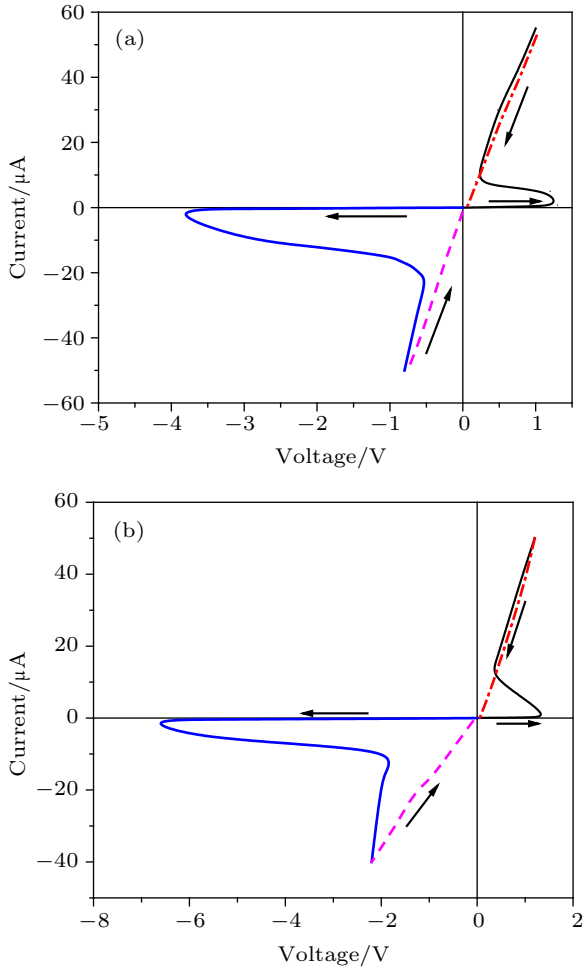


Fig. 3. (color online) (a) The *I–V* characteristics of the nonvolatile electric memory surface-type element based on organic semiconductors CuPc and H_2Pc (gap between Ag and Cu films is 30 μm). (b) The *I–V* characteristics of the nonvolatile electric memory surface-type element based on organic semiconductors CuPc and H_2Pc (the gap between Ag and Cu films is 40 μm).

Figure 4 shows the resistance-time relationship for the device with a 30-μm gap in a switching interval of 1 h. The resistance–time relationships for the devices with a 40-μm gap are approximately the same. On average the values of the resistances of the memory elements with a gap of 30 μm at high and low resistance states are 2402 kΩ and 21 kΩ, respectively. For the memory elements with a gap of 40 μm the values of

the resistances at high and low resistance states are 3752 kΩ and 25 kΩ, respectively. The ratios between the resistance at the high resistance state and that at the low resistance state are 120 and 150 for the devices with 30-μm and 40-μm gaps, respectively. Under the switching condition, the current increases ∼ 80–100 times. It is observed that the retention time is larger than 25 h, the read cycle (read time or response time) is smaller than μs, and endurance is larger than 1200 cycles.

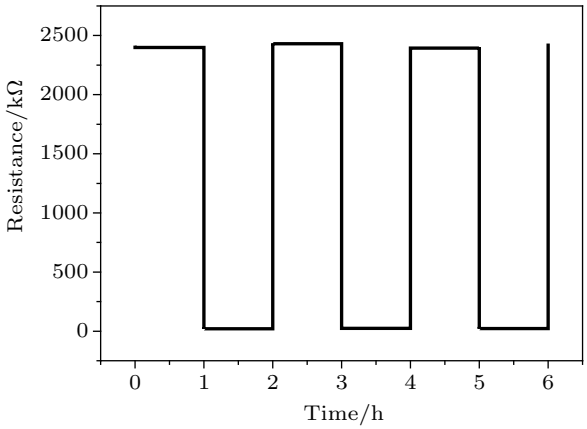


Fig. 4. Resistance–time relationships (in a switching interval of 1 h) for the nonvolatile electric memory surface-type element based on organic semiconductors CuPc and H_2Pc (the gap between Ag and Cu films is 30 μm).

By using the energy band diagrams developed for metal–semiconductor and semiconductor–semiconductor heterojunctions,[23] the properties of the CuPc and H_2Pc memory element can be explained. Figure 5 shows the energy band diagrams of the metal (Cu or Ag) and p-semiconductor junction (CuPc) (Fig. 5(a)) and heterojunction (CuPc and H_2Pc junction) (Fig. 5(b)) under thermal equilibrium condition. Taking into account the fact that CuPc and H_2Pc are p-type semiconductors and their work functions (3.87 eV and 4.04 eV) are lower than the work functions of Cu and Ag (4.65 eV and 4.26 eV), we can consider that CuPc and Cu or Ag contacts are ohmic (Fig. 5(a)). At the same time, semiconductor–semiconductor (CuPc–H_2Pc) heterojunction (Fig. 5(b)) is much more complicated at the interface of the semiconductors. From the CuPc side an enhancement region is seen, whereas from the side of the H_2Pc a depletion region is observed. If the voltages are applied to the terminals of the memory element, one of the CuPc–H_2Pc junctions will be forward biased and the other will be reversely biased. The total resistance of the path CuPc–H_2Pc–CuPc will depend on the reverse bias region as it has higher resistance than the forward bias region. Therefore, this path can provide symmetric *I–V* characteristics. The second path Ag–CuPc–Cu is due to the differences between Ag and Cu work functions that are responsible for the asymmetric behavior in the *I–V* characteristic. We assume that this effect takes place due to easier transfer and accumulation of charges from metal to the CuPc potential well which has essentially different depths as seen in Fig. 5(a). The NDR observed in the *I–V* characteristic is probably due to the sharp increase in the concentration of charges or mobility under the effect of the applied voltage. As in the organic semiconductors the hopping mechanism of conduction is observed,[24,25] it can be considered that each molecule acts as a potential well. Under the effect of electric field it can be assumed that the barrier between potential wells becomes smaller and thinner that can result in the increases of concentration and mobility of the charge carriers.

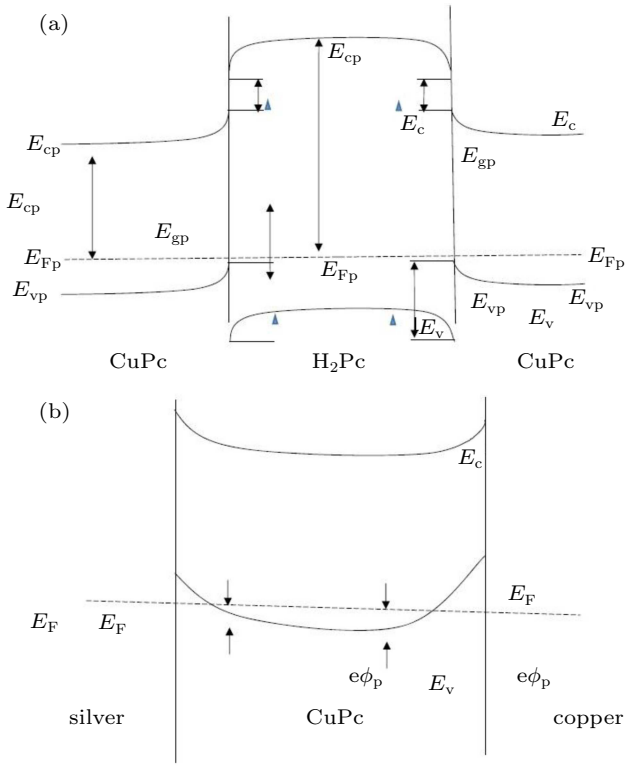


Fig. 5. Energy band diagrams of metal (Cu or Ag) and p-semiconductor junction (CuPc) (a) and the p–p heterojunction (CuPc and H_2Pc junction) (b) under thermal equilibrium.

4. Conclusions

In this work, the surface-type memory elements are fabricated based on organic semiconductors CuPc and H_2Pc whereas Cu and Ag are used as electrodes. In the *I–V* characteristics, the nonvolatile memory effect, switching effect, and negative differential resistance region are observed. The switching mechanism is attributed to electric-field-induced charge transfer from a low- to a high-conductivity state and back to a low conductivity state if the opposite polarity voltage is applied. The *I–V* characteristics show a rectifying behavior.

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