Multi-polar resistance switching and memory effect in copper phthalocyanine junctions*

Qiao Shi-Zhu(乔士柱)[a], Kang Shi-Shou(康仕寿)[a]†, Qin Yu-Feng(秦羽丰)[b], Li Qiang(李 强)[a], Zhong Hai(钟 海)[a], Kang Yun(康 韵)[a], Yu Shu-Yun(于淑云)[a], Han Guang-Bing(韩广兵)[a], Yan Shi-Shen(颜世申)[a], and Mei Liang-Mo(梅良模)[a]

[a] *School of Physics and State Key Lab of Crystal Materials, Shandong University, Jinan* 250100, *China*
[b] *Department of Applied Physics, School of Information Science and Engineering, Shandong Agricultural University, Taian* 271018, *China*

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Copper phthalocyanine junctions, fabricated by magnetron sputtering and evaporating methods, show multi-polar (unipolar and bipolar) resistance switching and the memory effect. The multi-polar resistance switching has not been observed simultaneously in one organic material before. With both electrodes being cobalt, the unipolar resistance switching is universal. The high resistance state is switched to the low resistance state when the bias reaches the set voltage. Generally, the set voltage increases with the thickness of copper phthalocyanine and decreases with increasing dwell time of bias. Moreover, the low resistance state could be switched to the high resistance state by absorbing the phonon energy. The stability of the low resistance state could be tuned by different electrodes. In Au/copper phthalocyanine/Co system, the low resistance state is far more stable, and the bipolar resistance switching is found. Temperature dependence of electrical transport measurements demonstrates that there are no obvious differences in the electrical transport mechanism before and after the resistance switching. They fit quite well with Mott variable range hopping theory. The effect of Al_2O_3 on the resistance switching is excluded by control experiments. The holes trapping and detrapping in copper phthalocyanine layer are responsible for the resistance switching, and the interfacial effect between electrodes and copper phthalocyanine layer affects the memory effect.

Keywords: organic memory, resistance switching, copper phthalocyanine

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1. Introduction

Organic materials, because of the advantages such as low cost fabrication, printability, high mechanical flexibility, and environment friendly, are being successfully used in organic light-emitting display (OLED), field effect transistor and solar cell fields.[1–6] Recently, the organic memory devices have inspired more and more attention for their potential use in substituting inorganic ones to satisfy the demand for inexpensive and high density data storage media.[7–15] Many organic materials including small molecular and polymer have achieved the memory effect.[7–15] Reddy *et al*. found bias-symmetrical unipolar resistance switching effect in indium tin oxide/ tris-(8-hydroxy-quinoline)aluminum(Alq_3)/Al nanoparticles/Alq_3/Al system.[16] They believed that the charge transfer between Alq_3 and Al nanoparticles induced by the electrical field was responsible for the resistance switching. Al_2O_3 was also thought to be very important for the resistance switching.[10,16,17] The bipolar resistance switching behavior was achieved in a Cu/Cu: tetracyanoquinodimethane(TCNQ)/Al device by Kever *et al*.[17] They ascribed the switching behavior to copper ions based on the electrochemical effect in naturally formed aluminum oxide. They also speculated that the TCNQ was not essential for the switching process and just acted as a spacer. Meanwhile, nonpolar resistance switching was also reported.[14] However, multi-polar (unipolar, bipolar and nonpolar) switching behaviors have not been observed simultaneously in one organic material before. Different explanations for many kinds of resistance switching indicated that the mechanism behind the resistance switching and memory effect was still under debate.[18] Molecular structure, interfacial effect and electrode property could significantly affect the resistance switching behavior and memory effect, leading to the need for more experimental and theoretical work.

Previous research on resistance switching and memory effect in small molecular systems includes Alq_3, TCNQ, copper−2,3-dichloro-5,6-dicyano-p-benzoquinone, etc.[7,17,19] However, little attention was paid to copper phthalocyanine (CuPc), a prototypical conjugate p-type organic semiconductor and widely used in OLED,[20] diodes,[21] organic thin film transistors,[22] and organic photovoltaic cells.[23] CuPc junctions, successfully achieving tunnel-

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†Corresponding author. E-mail: skang@sdu.edu.cn

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ing magnetoresistance,[24] may be used for spin-polarized OLED,[25] spin field-effect transistors,[26] and sensors.[27] In this work, the multi-polar (including unipolar and bipolar) resistance switching and memory effect were achieved in the CuPc junctions with different electrodes, which may be applied to organic memory devices. The thickness dependence of resistance switching and memory effect was studied. The impact of Al_2O_3 on resistance switching was excluded by control experiments. The temperature dependence of resistance before and after switching were characterized and analyzed with variable range hopping theory. The stability of low resistance state was tuned by different electrodes. The mechanism of multi-polar resistance switching and memory effect was also investigated.

2. Experiment

As illustrated in Fig. 1, a bottom electrode consisting of Ta (2 nm), Ag (10 nm), Co (5 nm) and a top electrode consisting of Co (20 nm), Ag (20 nm) of CuPc junctions were deposited onto the glass substrates using a shadow mask by magnetron sputtering with a base pressure of 1×10^{-7} Torr. The CuPc layer (with the thickness ranging from 5 nm to 20 nm) was grown by thermal evaporation at a rate of 0.1 Å/s after deposition of the bottom electrode. Then, a 1-nm Al layer was sputtered on the surface of CuPc and further oxidized by the oxygen plasma *in situ* to form a layer of Al_2O_3, which prevented the diffusion of the top electrode and enhanced resistance of the junctions.[7] The active junction size was determined by the cross area of top and bottom electrodes, which was 0.1×0.1 mm^2.

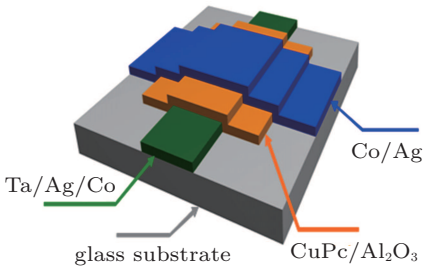


Fig. 1. (color online) Schematic of CuPc junctions.

The current–voltage (I–V) characteristics of the CuPc junctions were measured by using a Keithley 2400 source meter and a Keithley 2182 nanovoltmeter interfaced to a computer. The low temperature measurements were achieved in a cryogen provided by SQUID. The bias polarity was defined with respect to the top electrode.

3. Results and discussion

It is universal that junctions with a thickness of CuPc ranging from 5 nm to 20 nm show distinct resistance switching behaviors. Figure 2 illustrates the typical I–V characteristics of CuPc junctions with different thicknesses. The bias increases from zero to the maximum value and then decreases back to zero. Initially, all junctions are at the high resistance state (HRS) with resistance at the magnitude of millions of ohm. When the bias reaches the set voltage (V_{set}), the junctions are switched to the low resistance state (LRS) abruptly, with resistance ranging from several hundreds ohm to tens of thousands of ohm. Here a compliant current is kept constant in order to protect junctions from overheating. Generally, V_{set} increases with the thickness of CuPc. The resistance ratio of HRS and LRS is from at least 10^2 even up to 10^5, which is distinct among the recent resistance switching memory devices.[9,11,16] Such resistance switching could be repeated for several to dozens of times based on different junctions before they are shortened.

Figure 3 shows the behaviors of LRS in different CuPc junctions under the bias of 1 mV. As we can see, the current abruptly decreases by several magnitudes at the time t_s, indicating the transition from LRS to HRS. The fluctuation of the resistance in HRS is mainly due to the precision limitation of our measurements. This transition may be related to the electron–phonon coupling and will be discussed later. Generally, t_s increases with the thickness of CuPc layer, although a few exceptions indeed exist.

Other kinds of unipolar resistance switching behaviors are also observed. Figure 4(a) demonstrates the resistance switching behavior of the junction with 15-nm CuPc. The sweeping rate of the bias voltage is 50 mV/step. At the end of the first sweep, the junction is in the LRS, but at the beginning of the second sweep, the junction is switched back to the HRS. Figure 4(c) shows another type of resistance switching. Unlike the former, the LRS in Fig. 4(c) is switched back to the HRS when the bias is swept back. These three kinds of resistance switching behaviors are very common in all CuPc junctions. Figures 4(b)–4(d) show the sweeping rate dependence of V_{set} for the junction with 20 nm CuPc. It is clear that the V_{set} is strongly dependent on the bias sweeping rate.

We also study the electrical transport characteristic of the junction with 20 nm CuPc, as shown in Figs. 5(a) and 5(b). The resistance of both HRS and LRS increases with decreasing temperature. The organic semiconductor, unlike its counterpart inorganic semiconductor which has a long-range order and strong coupling between the lattices, has a weak Van Der Waals interaction between unit cells leading to the strong localization of the charge carriers. The charge carriers could not contribute to the conduction until they hop to another unit cell by absorbing enough phonon energy, which results in the low mobility of organic materials. Mott found a model to explain the charge transport problem in the low-mobility materials called the variable-range hopping equation, $\log G \sim T^{-\gamma}$,

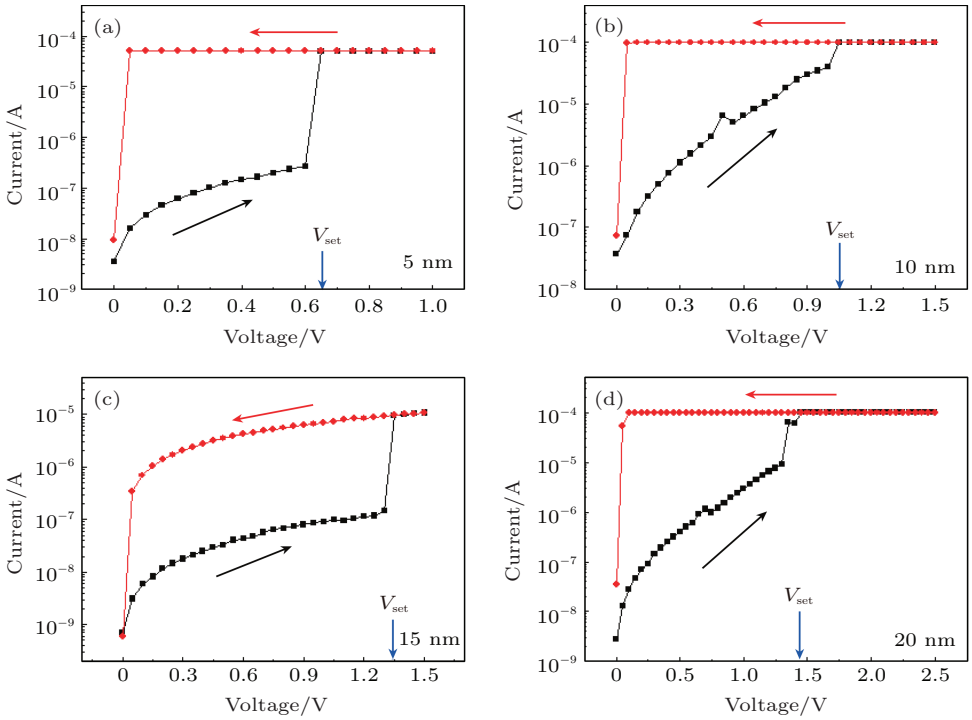


Fig. 2. (color online) Resistance switching behaviors of Ta/Ag/Co/CuPc/Al_2O_3/Co/Ag junctions with different thickness of CuPc: (a) 5 nm, (b) 10 nm, (c) 15 nm, and (d) 20 nm. The arrows indicate the bias sweeping directions.

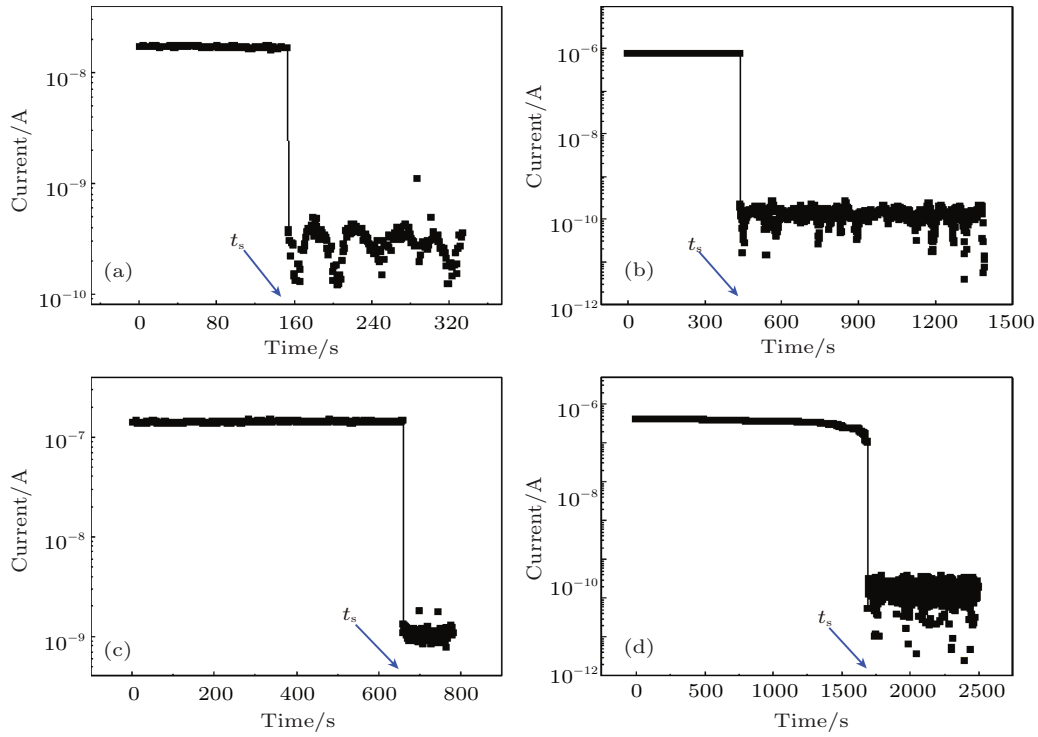


Fig. 3. (color online) Time dependence of resistance for the junctions with different thicknesses of CuPc layer: (a) 5 nm, (b) 10 nm, (c) 15 nm, and (d) 20 nm.

where $\gamma = 1/4$, G is the conductance and T is the absolute temperature.[28] Roth and Bleier further developed this theory and found that $\gamma = 1/3$ is more suitable for 2D systems.[29] Figures 5(c) and 5(d) show the ln$G$–$T^{-1/3}$ relation of the HRS and LRS in CuPc junctions. Blue lines are the linear fitting curves, which demonstrate a good agreement with variable-range hopping theory at the low temperature. The slope k of blue line and the density of state at Fermi level N_F have such relation, $N_F \propto -1/k^3$.[29] The slopes of HRS and LRS are about -15.3 and -1.3, respectively, so the N_F ratio of LRS and HRS is about 1600, leading to the huge difference in resistance as shown in Figs. 5(a) and 5(b).

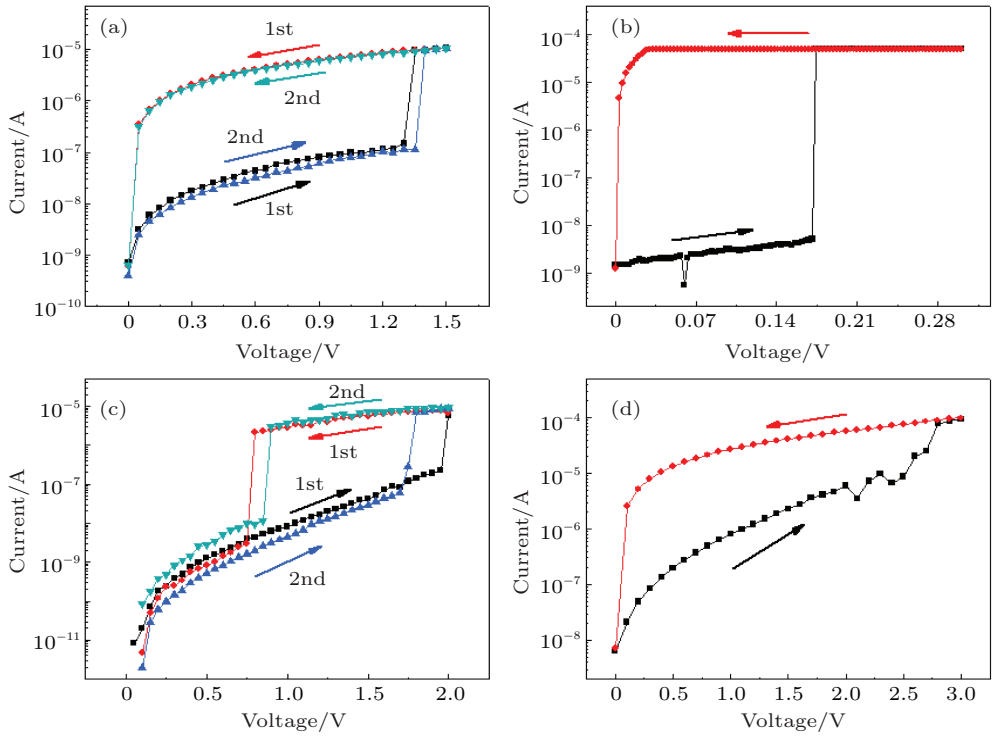


Fig. 4. (color online) *I–V* curves of Ta/Ag/Co/CuPc/Al_2O_3/Co/Ag junctions with different thickness of CuPc layer and different sweeping rate of bias. (a) 15 nm, 50 mV/step; (b) 20 nm, 3 mV/step; (c) 20 nm, 50 mV/step; and (d) 20 nm, 100 mV/step.

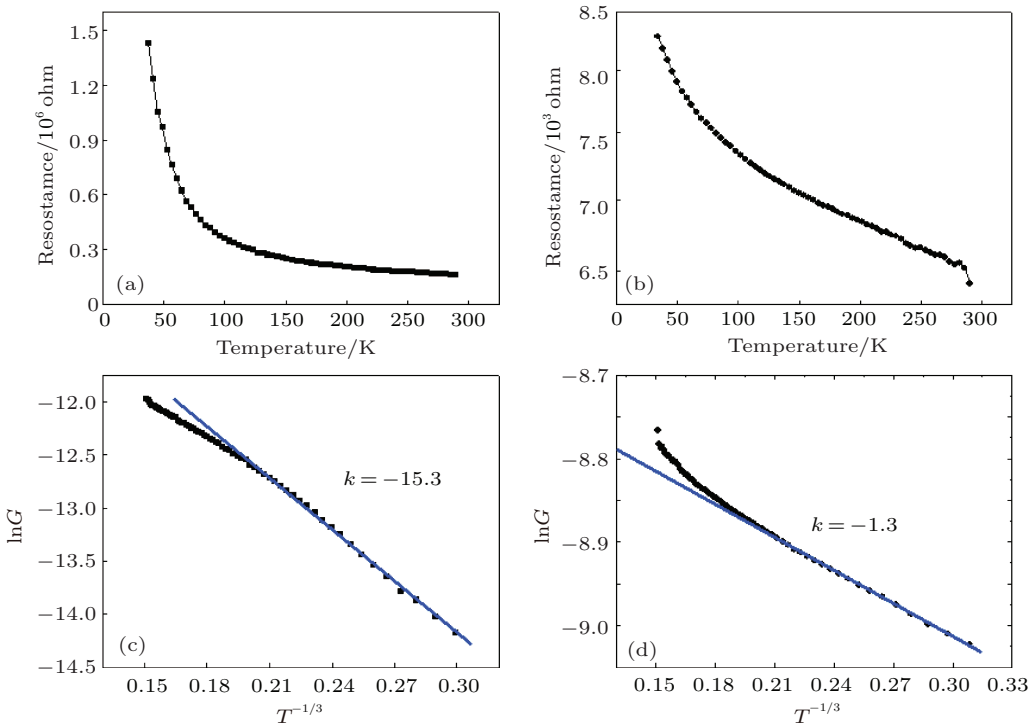


Fig. 5. (color online) Resistance–temperature characteristics of (a) the HRS and (b) the LRS; ln$G$ and $T^{-1/3}$ relation and liner fitting curves of (c) the HRS and (d) the LRS. G is the conductance, T is the temperature, and k is the slope.

In order to find out the mechanism behind resistance switching and memory effect, and increase the stability of LRS, we change the bottom electrode with Au instead of Ta/Ag/Co. Figure 6(a) shows the *I–V* curve of the Au(20)/CuPc(20)/Al_2O_3(1)/Co(20)/Ag(20) junction and the inset in Fig. 6(a) illustrates the time dependence of the LRS under the bias of 10 mV. Unlike the Ta/Ag/Co/CuPc/Al_2O_3/Co/Ag junction with a unipolar resistance switching, this junction clearly shows a bipolar switching behavior. When the bias is swept in negative field (see step

1 in Fig. 6(a)), the junction is switched from the HRS to LRS at a bias of −1.3 V, and the junction stays on LRS after the bias is swept back to zero. The resistance of LRS does not have an evident degradation even under the bias of 10 mV for more than 10^4 seconds (see the inset of Fig. 6(a)), compared to CuPc junctions with Co–Co electrodes measured under 1 mV, due to the fact that higher voltage is more likely to switch LRS to HRS. Only the positive bias sweeping could lead the switch from the LRS to HRS as illustrated in Fig. 6(a) (step 3). Obviously, the HRS is more stable under the positive bias, and it is hard to be switched back to the LRS with the positive bias. Bipolar switching is also found in a Au/CuPc/Co/Ag device without any Al_2O_3 layer, but the LRS is less stable and resistance switching behavior like Fig. 6(b) occurs occasionally. Therefore, the barriers between electrodes and CuPc are important for bipolar switching and the stability of LRS.

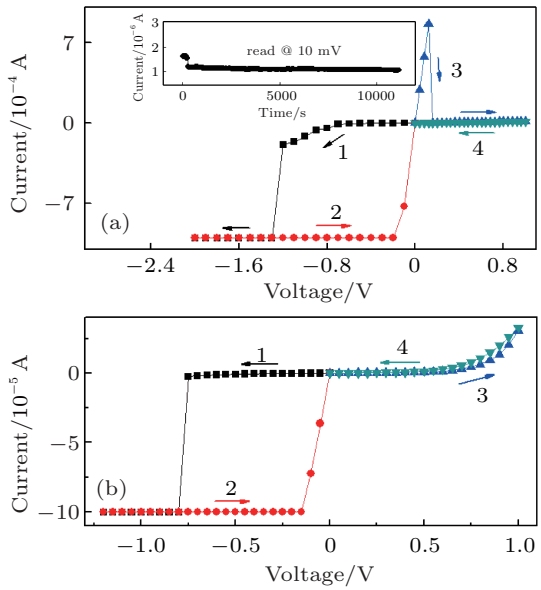


Fig. 6. (color online) Resistance switching behavior of (a) Au/CuPc/Al_2O_3/Co/Ag junction. Inset: the time dependence of LRS under the bias of 10 mV, and (b) Au/CuPc/Co/Ag junction.

As shown in Figs. 7(a) and 7(b), the resistance switching also occurs in the Au/CuPc/Au and Ta/Ag/Co/CuPc/Co/Ag systems fabricated by the same method (see Section 2). In these CuPc junctions, neither Al nor Al_2O_3 is used. Thus, the impact of Al_2O_3 on resistance switching is completely ruled out.[30–32] The above results clearly demonstrate that the resistance switching behavior is so prevalent in all CuPc junctions no matter what electrodes are, convincing us that this resistance switching behavior is the property of CuPc layer.

Metal electrode filament mechanisms were often used to explain the switching behavior,[18,33,34] where an electrode's cations drift into the middle layer because of the strong electrical field, forming or breaking metal dendrites connecting the top and bottom electrodes and leading to the LRS or HRS, respectively. However, it is unsuitable for explaining our results. Firstly, the resistance-temperature curve of the LRS in Fig. 5(b) is obviously not related to the metal conduction mechanism. Secondly, the resistance of the LRS of junctions with 20-nm CuPc decreases with increasing junction size, as shown in Fig. 8(a). Here each point represents an average value of 10 different junctions. In general, for a metal filament mechanism, as shown schematically in Fig. 8(b), once a metal filament reaches the top electrode, the electric field in organic material decays rapidly, because the junction is shortened, and the other metal dendrites stop growing. The resistance of LRS mainly depends on the one metal filament which reaches the top electrode, so the resistance of LRS is independent of junction size, though the quantity of metal dendrites does increase with the junction size. Waser *et al*. reported very similar results.[33]

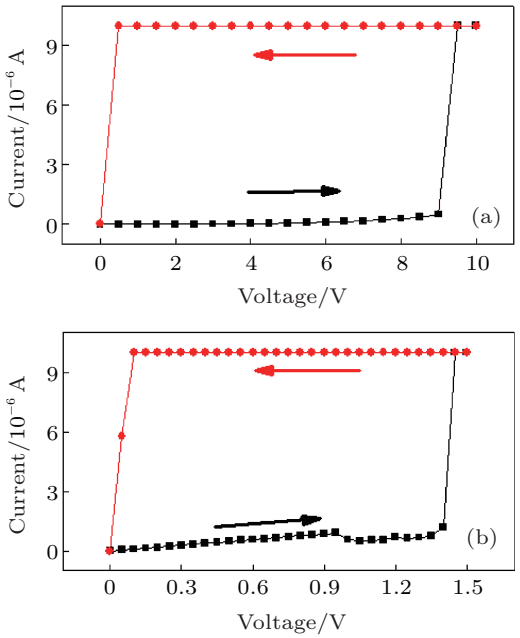


Fig. 7. (color online) Resistance switching behaviors of (a) Au(20)/CuPc(20)/Au(20) and (b) Ta(2)/Ag(10)/Co(5)/CuPc(20)/Co(20)/Ag(20).

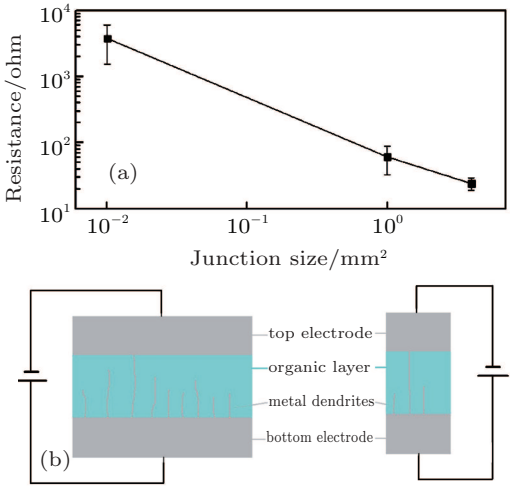


Fig. 8. (color online) (a) Relationship between the resistance of LRS and junction size. Each point represents an average value of 10 different junctions. (b) Schematic of metal dendrites on the LRS of metal filament mechanism.

The results presented above prove that the multi-polar resistance switching behavior and memory effect are the property of CuPc layer. The mechanism could be explained as the following.[14] As shown in Fig. 9(a), when a bias is applied, the holes are injected into CuPc due to the strong electrical field and stay in the trap states. When trap states are filled, making CuPc more conductive, the HRS is switched to the LRS. These holes-filled trap states are not stable without the bias applied,[35] and filled trap states could easily be detrapped. In an article by Yoshihiko,[36] the LRS of Ag/poly (N-vinylcarbazole)/Ag junction switched to HRS when the sample was heated above ~ 80 °C, which makes us speculate that the detrapping process may be assisted by phonon energy, although the details of this process need to be further studied. Once these holes escape from the trap states into the electrode, the LRS is switched back to the HRS, as shown in Fig. 9(b). This occurs in Ta/Ag/Co/CuPc/Al_2O_3/Co/Ag systems. However, for a Au/CuPc/Al_2O_3/Co/Ag system, the holes could be hardly injected into the CuPc under the low positive bias due to the interface dipole[37] between Au/CuPc. This could be verified in Fig. 7(a), where the resistance switching from the HRS to LRS occurred at 9.5 V. Interface dipole may originate from several contributions, such as the reduction of Au work function caused by CuPc, the reduction of CuPc band gap near Au/CuPc interface caused by image charge potential, the CuPc energetically distributed valence states and band bending, the chemisorptions and charge transfer between Au and CuPc,[38] and/or the gradient of the CuPc intermolecular interaction along the surface normal, which is due to the continuous increase in the molecular tilt angle with the film thickness.[39] The holes could be injected into CuPc under negative bias by tunneling through Al_2O_3, and got stuck in the trap states, leading the switch of HRS to LRS as illustrated in Fig. 9(c). In this case, the holes could not escape from the trap states only by absorbing phonon energy since both sides of the CuPc were barriers. Hence, the system stays in the LRS. Only positive bias could extract the holes from trap states and the LRS is switched back to the HRS (see Fig. 9(d)).

The thickness dependence of V_{set} and t_s in Figs. 2–4 could be explained as follows. The barrier between the electrode and trap states increases with the thickness of CuPc. For the thicker junctions, the holes need more energy (higher V_{set}) or longer time (smaller bias sweeping rate) to fully occupy the trap states and lead the switching from the HRS to LRS. Similarly, the holes need a longer time (t_s) to absorb enough phonon energy to fully escape from the trap states and lead the switching from the LRS to HRS.

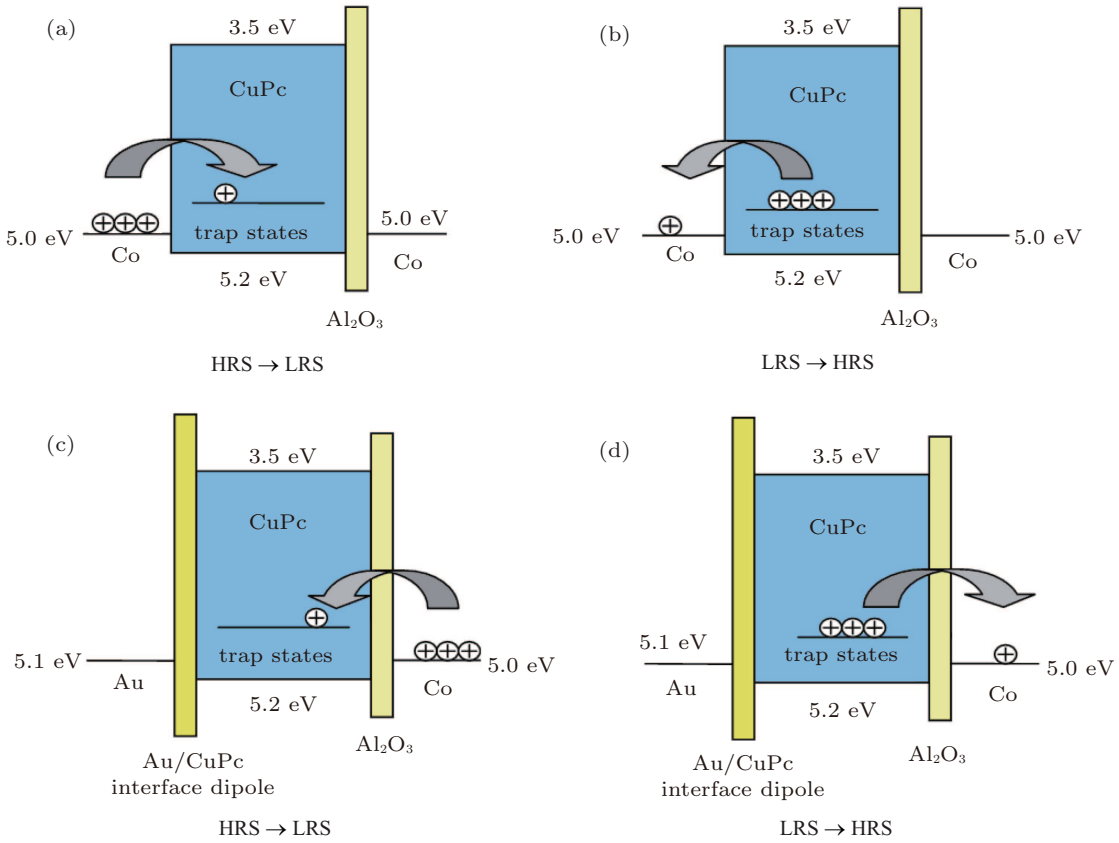


Fig. 9. (color online) Schematic diagram of the resistance switching in Ta/Ag/Co/CuPc/Al_2O_3/Co/Ag junction: (a) holes injection under the positive bias and trapped in trap states; (b) holes detrapping by absorbing phonon energy. Schematic diagram of the resistance switching in Au/CuPc/Al_2O_3/Co/Ag junction; (c) holes injection under the negative bias; and (d) holes detrapping under the positive bias. The work function of Co and Au are 5.0 eV and 5.1 eV, the LUMO and HOMO of CuPc are 3.5 eV and 5.2 eV, and $\oplus$ denotes holes.

4. Conclusion

In this work, the multi-polar resistance switching and memory effect in CuPc junctions have been demonstrated. In a Ta/Ag/Co/CuPc/Al_2O_3/Co/Ag system, the unipolar resistance switching behavior is prevalent with the different thickness of CuPc, ranging from 5 nm to 20 nm. The V_{set} of resistance switching from the HRS to LRS increases with the CuPc thickness. Increasing the dwell time of bias and/or decreasing bias sweeping rate could decrease the V_{set}. The LRS could be switched back to the HRS by absorbing the phonon energy. The temperature-resistance study of the HRS and LRS reveals that the conduction mechanism of charge carriers is the same for the junctions before and after the resistance switching. They all fit quite well with Mott variable range hopping theory and could exhibit the different density of state at Fermi level for the LRS and HRS. The Au/CuPc/Al_2O_3/Co/Ag system shows a bipolar switching behavior with a more stable LRS, which is caused by Au/CuPc interface dipole. Control experiments rule out the impact of Al_2O_3 on the resistance switching. We believe that resistance switching is a property of the CuPc layer and closely related to the holes trapping and de-trapping in the CuPc layer.

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