Inorg. Chem. **2007**, *46*, 341–344

Inorganic Chemistry

Article

Negative Differential Resistance and Memory Effect in Diodes Based on 1,4-Dibenzyl C60 and Zinc Phthalocyanine Doped Polystyrene Hybrid Material

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Received September 27, 2006

Negative differential resistance (NDR) and memory effect were observed in diodes based on 1,4-dibenzyl C60 (DBC) and zinc phthalocyanine doped polystyrene hybrid material. Certain negative starting sweeping voltages led to a reproducible NDR, making the hybrid material a promising candidate in memory devices. It was found that the introduction of DBC enhanced the ON/OFF current ratio and significantly improved the memory stability. The ON/OFF current ratio was up to 2 orders of magnitude. The write–read–erase–reread cycles were more than 10^6, and the retention time reached 10 000 s without current degradation.

Introduction

Negative differential resistance (NDR) devices have attracted considerable attention for their tremendous potential applications in low-power memory and logic circuits.[1−4] In these NDR devices, the current−voltage characteristics generally show a region in which the current decreases with an increase of the voltage. At present, the successful demonstrations of NDR suitable for memory and circuit applications are restricted to rigid inorganic semiconductors.[5,6] As is known, smartcards, such as banking and medical information, are expected to be flexible with low power. It is well-known that organic and polymeric materials are uniquely suited for thin, flexible, and low-power electronic devices.[7−10] Recently, the realization of NDR based on organic molecules and polymers has intrigued researchers, but it has not been demonstrated successfully yet because of their lack of stability.[11−14]

In this paper, we demonstrate a stable NDR and memory effect in electrical conduction from a hybrid material containing 1,4-dibenzyl C60 (DBC) and zinc phthalocyanine (ZnPc) doped with polystyrene (PS). The mixture is solution-processible; thus, the devices can be fabricated by a simple spin-coating method. A large reproducible and stable NDR behavior was obtained, and the stability was greatly improved as a result of the doping of DBC.

Experimental Section

The DBC used was synthesized and purified in our laboratory as described in the literature.[15] Our diodes consist of a spin-coated polymer layer between two electrodes. The bottom electrode is indium−tin oxide (ITO). The typical polymer layer was formed

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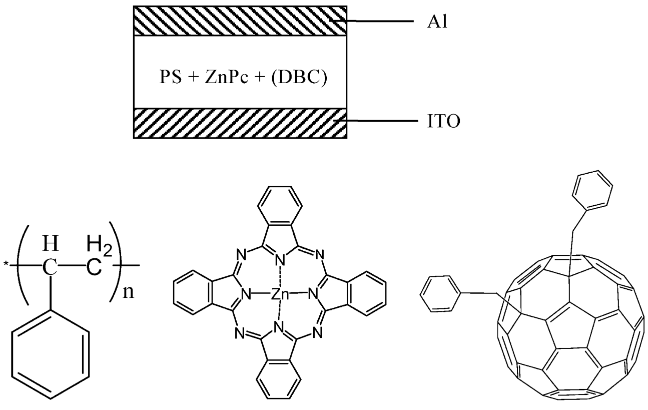
10.1021/ic061851w CCC: $37.00
Published on Web 01/02/2007



PS ZnPc DBC

Figure 1. Device structure and molecular structures of the materials used.

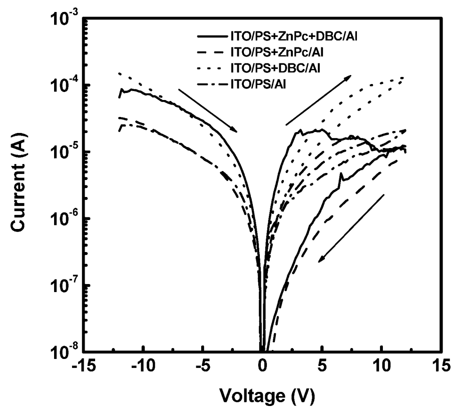


Figure 2. $I-V$ characteristics of ITO/PS:ZnPc/Al, ITO/PS:ZnPc:DBC/Al, ITO/PS:DBC/Al, and ITO/PS /Al devices at a −12 V starting sweeping voltage.

by spin-coating a solution of 0.67 wt % PS (M_w = 250 000), 0.18 wt % ZnPc, and 0.025 wt % DBC onto a precleaned ITO glass substrate. The top Al electrode was thermally evaporated with a vacuum of 10^{-4} Pa. The devices had an active area of 3 × 3 mm^2. For comparison, ITO/PS/Al, ITO/PS:ZnPc/Al, and ITO/PS:DBC/Al devices were also fabricated by using the same conditions. Each structure of the devices was prepared 10 times, and thus 40 devices for each structure were evaluated. The current−voltage ($I-V$) characteristics and the write−read−erase−reread (WRER) cycles were performed by a Keithley 2400 sourcemeter controlled by a computer. All electrical measurements were carried out under ambient conditions at room temperature without any device encapsulation. Figure 1 shows the device structure and the molecular structures of the materials used.

Results and Discussion

It was found experimentally that a ITO/PS:ZnPc/Al device shows NDR in the $I-V$ characteristics in the region of positive bias (ITO as the cathode and Al as the anode) as the start voltage is swept from certain negative values. Figure 2 shows the $I-V$ characteristics of ITO/PS:ZnPc/Al at a −12 V starting sweeping voltage. It can be seen in the forward region that the current is initially high and increases with the bias voltage. As the voltage arrives at 8 V, the current reaches a maximum value and then decreases to form the NDR region. As the bias voltage is swept from 12 to 0 V, the current remains at a lower conductance state. This

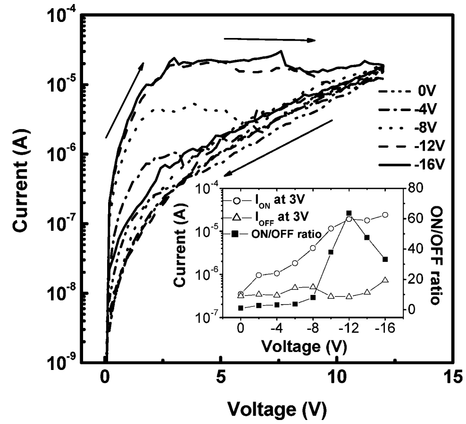


Figure 3. Forward $I-V$ characteristics of the ITO/PS:ZnPc:DBC/Al device at different negative sweeping voltages. The ON state and OFF currents at 3 V and the ON/OFF current ratio as a function of the negative sweeping voltages are shown in the inset.

behavior, in which a high conductance current and a low conductance current exist simultaneously at the same voltage, is ideal for memory applications. However, as shown below, ITO/PS:ZnPc/Al exhibits poor NDR stability. We found that doping a C60 derivative DBC into PS:ZnPc to fabricate ITO/PS:ZnPc:DBC/Al devices not only enhances the current ratio between the high conductance state and the low conductance state but also greatly improves the NDR stability. A typical $I-V$ characteristic of ITO/PS:ZnPc:DBC/Al with a −12 V starting sweeping voltage is shown in Figure 2. It can seen that the same NDR characteristic is obtained with a larger current ratio in ITO/PS:ZnPc:DBC/Al devices. For comparison, the $I-V$ characteristics of ITO/PS/Al and ITO/PS:DBC/Al devices are also shown in Figure 2. No NDR is observed in ITO/PS/Al and ITO/PS:DBC/Al. This indicates that ZnPc and DBC in ITO/PS:ZnPc/Al and ITO/PS:ZnPc:DBC/Al play important roles in NDR formation.

Significant features of ITO/PS:ZnPc/Al and ITO/PS:ZnPc:DBC/Al devices are that the low conductance state can be recovered to a high conductance state by simply applying a negative bias voltage or the high conductance state can be returned to a low conductance state by applying a forward bias voltage, and it was found that the current ratio between the high conductance state (ON) and the low conductance state (OFF) is strongly dependent on the magnitude of the applied negative sweeping voltage. Figure 3 shows the forward $I-V$ characteristic of the ITO/PS:ZnPc:DBC/Al device at different negative sweeping voltages. It is clearly seen that the negative sweeping voltages increase the ON state current and make the current saturated with the sweeping voltage. However, the negative sweeping voltages show a weak effect on the OFF current. As a result, the ON/OFF current ratio shows the largest value with the negative sweeping voltage. The inset of Figure 3 shows the ON state and OFF currents at 3 V and the ON/OFF current ratio as a function of the negative sweeping voltages. This indicates that the ON/OFF current ratio can be controlled by the magnitude of the applied negative sweeping voltage.

The reproducible NDR in the $I-V$ characteristics defines the electrical bistability of diodes and also reveals the nonvolatile nature of the memory effect in diodes used as

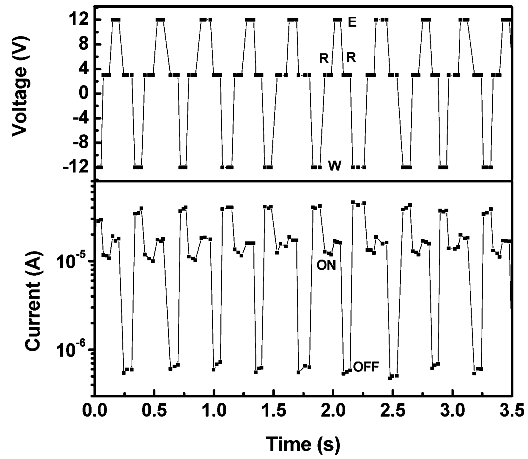


Figure 4. Current response of the ITO/PS:ZnPc:DBC/Al device during WRER voltage cycles.

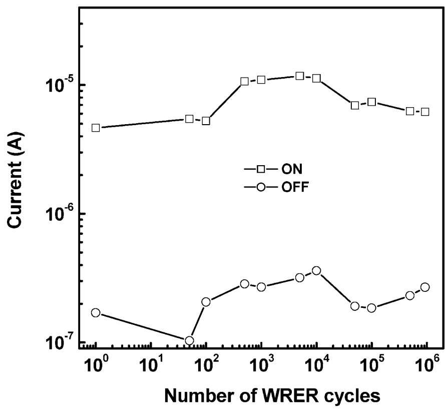


Figure 5. Current in the ON and OFF states as a function of the number of WRER cycles of the ITO/PS:ZnPc:DBC/Al device.

two-terminal memory cells that can be written and erased by high negative voltage and high positive voltage, respectively, and read out by low positive voltage. To demonstrate the applicability of ITO/PS:ZnPc:DBC/Al as memory devices, WRER cycle characteristics of the devices were measured. Figure 4 shows the current response of the ITO/PS:ZnPc:DBC/Al device during WRER voltage cycles. The voltages for WRER cycles were −12, 3, 12, and 3 V, respectively. As can be seen, a voltage of −12 V was applied to switch the device to the high ON state. If we designate "1" as the ON state and "0" as the OFF state, the "1" state is then written. The "1" state could be read by a low forward voltage (3 V) with a current on the order of 10^{-5} A. The ON state could be erased by applying a forward bias of 12 V to produce the OFF state, and then the "0" state could be reread by a forward voltage of 3 V with a current on the order of 10^{-7} A. As shown in Figure 5, where the current in the ON and OFF states is given as a function of the number of WRER cycles of the ITO/PS:ZnPc:DBC/Al device, more than 10^6 WRER cycles are conducted on the device without any significant current degradation.

The ITO/PS:ZnPc:DBC/Al devices also show better stability in both conductivity states. The data retention characteristics in the ON and OFF states of ITO/PS:ZnPc:DBC/Al are shown in Figure 6. For comparison, the retention characteristics of ITO/PS:ZnPc/Al device are also shown in

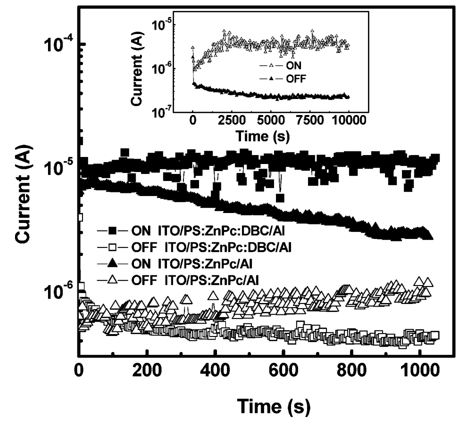


Figure 6. Comparison of the data retention characteristics in the ON and OFF states of ITO/PS:ZnPc:DBC/Al and ITO/PS:ZnPc/Al. The data retention characteristics for 10 000 s in the ON and OFF states of ITO/PS:ZnPc:DBC/Al are shown in the inset.

Figure 6. The characteristics were performed by continuously applying a bias of 3 V to the device over prolonged periods of time. It is clearly seen that the ITO/PS:ZnPc:DBC/Al devices did not exhibit a remarkable change in ON and OFF current after 1000 s, whereas the ON and OFF current of ITO/PS:ZnPc/Al obviously decays. As shown in the inset of Figure 6, the ON and OFF current remined almost constant even after 10 000 s. It can be seen that the rewriting capability and long retention time are greatly important as the basic requirement necessary for practical memory applications.

To clearly explain the conduction mechanism through ITO/PS:ZnPc:DBC/Al devices, the $I-V$ curves in both ON and OFF states were analyzed. Figure 7a shows the $I-V$ characteristic of the ITO/PS:ZnPc:DBC/Al device in the ON state in coordinates log(I) vs log(V). It can be seen that a straight line with a slope of 1.8 was observed. This indicates that a space-charge-limited current is probably the main conduction mechanism in the ON state.[16] The $I-V$ characteristic changed after the electrical transition to the OFF state. A linear relationship was observed in a plot of log(I) vs $V^{1/2}$ in the OFF state, as shown in Figure 7b. This suggests that after the transition the current through the device may change to thermionic emission.[16] The same $I-V$ curves in the ON and OFF states were also observed in ITO/PS:ZnPc/Al devices.

As is known, ZnPc is a planar-conjugated aromatic macrocycle molecule that can be used as an electron donor.[17] Therefore, in the case of ITO/PS:ZnPc/Al devices, as the reverse bias voltage is applied (ITO as the anode and Al as the cathode), ZnPc in the PS film will loss π electrons and be positively charged as a result of sufficient injection of the holes. The processes are similar to the chemical oxidation of organic molecules. It is well-known that the conductivity of organic molecules is greatly increased after chemical oxidation.[18] Therefore, in this case, the current is high as

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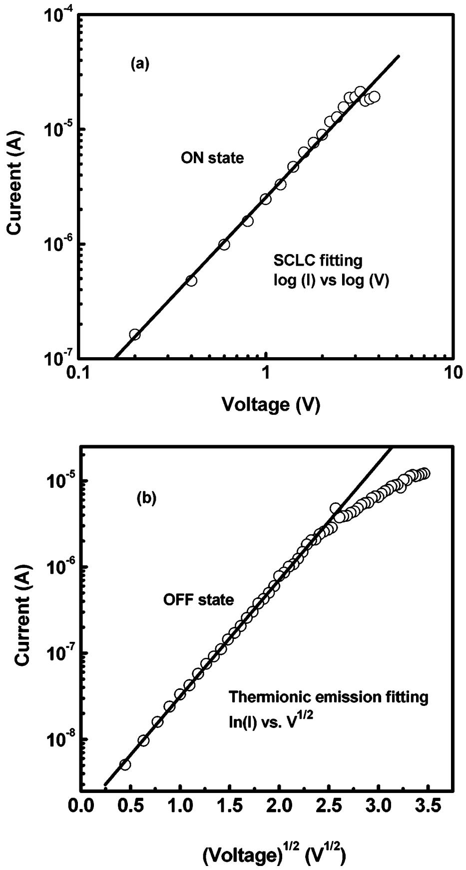

Figure 7. *I*−*V* characteristic of the ITO/PS:ZnPc:DBC/Al device in the ON state (a) and the OFF state (b).

the sweeping voltage goes to forward bias (ITO as the cathode and Al as the anode). With an increase of the forward bias voltage, the positive charges on ZnPc molecules will gradually consume as a result of the larger hole injection barrier at the Al anode; thus, the current decreases with the bias voltage, forming the NDR region. As the sweeping voltage goes to 0 V, the current remains in the low conductance state.

For the case of ITO/PS:ZnPc:DBC/Al devices, [60]-fullerene (C60) and its derivatives such as DBC are three-dimensional electron-acceptor materials.[19] When DBC is doped into PS containing donor ZnPc, therefore, besides the oxidation of ZnPc at an electrical field, the charge-transfer state between DBC and ZnPc molecules induced by an electrical field is also formed in the hybrid system. It is well-known that electrical-field-induced charge transfer in donor−acceptor systems is the main mechanism used to explain the electronic transition, and the formed charge-transfer state generally exhibits a higher conductivity.[20] A certain reverse bias voltage (ITO as the anode and Al as the cathode) then leads to the formation of a charge-transfer state between DBC and ZnPc; thus, the current shows a high conductance state as the sweeping voltage goes to the forward bias (ITO as the cathode and Al as the anode). However, the forward sweeping voltage can lead to a return of the charge-transfer state formed between DBC and ZnPc to its original state, resulting in NDR and a reduction of the current. It can be seen that the electrical-field-induced charge transfer between ZnPc and DBC molecules greatly improves the reproducibility of NDR and the retention time in memory devices.

Conclusion

We have demonstrated a large and reproducible NDR and memory effects in a hybrid material containing DBC and ZnPc doped with PS. It was found that the memory stability was greatly improved as a result of the introduction of DBC. The WRER cycles are more than 10^6, and the retention time reaches 10 000 s without current degradation. Our results indicate that DBC and ZnPc doped with PS hybrid material is a promising material system in memory applications.

Acknowledgment. The authors thank the Hundreds Talents program of Chinese Academy of Sciences, National Natural Foundation of China (Grant 50573075), the National Science Fund for Distinguished Young Scholars of China (Grant 50325312), and the Ministry of Science and Technology of China (973 Program No. 2002CB613403) for support of this research.

IC061851W

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