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Nonvolatile organic write-once-read-many-times memory devices based on hexadecafluoro-copper-phthalocyanine

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Nonvolatile organic write-once-read-many-times memory device was demonstrated based on hexadecafluoro-copper-phthalocyanine (F_{16} CuPc) single layer sandwiched between indium tin oxide (ITO) anode and Al cathode. The as fabricated device remains in ON state and it can be tuned to OFF state by applying a reverse bias. The ON/OFF current ratio of the device can reach up to 2.3×10^3 . Simultaneously, the device shows long-term storage stability and long retention time in air. The ON/OFF transition is attributed to the formation and destruction of the interfacial dipole layer in the ITO/F₁₆CuPc interface, and such a mechanism is different from previously reported ones. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4721518]

Organic memory devices have attracted a great deal of attention due to their simplicity in device structure, good scalability, low-cost potential, low-power operation, and large capacity for data storage.^{1–7} There are three types of organic memory devices: random access memory, read-writeerase-rewritable memory, and write-once-read-many-times (WORM) memory. Recently, WORM memory devices have gained rapid development for their potential application for permanently data storage, such as wireless identification tags, smart cards, and personal data depositories.8-16 However, the development of organic WORM memory devices is still in its early stage and high performance devices are desired especially the ones with simple structure and construction process. On the other hand, the mechanisms involved in organic WORM memory devices are still under debate. Teo et al.9 have demonstrated that the transition from the low conductivity state (OFF state) to the high conductivity state (ON state) in a polymer based device is attributed to the conformation change. Smith and Forrest¹⁰ and Wang et al.¹¹ have found, respectively, that the switch between the ON state and OFF state of the polyethylene dioxythiophene:polysterene based devices is resulted from the oxidation/reduction reaction. Choi et al.¹² have proved that the WORM memory behavior of hyperbranched copper phthalocyanine based devices is due to the filament. Lin and Ma¹³ and Park *et al.*¹⁴ have proposed, respectively, that the memory effect is governed by the charge trapping in the active organic materials. Song et al.¹⁵ have argued that the charge-transfer complex formation between fluorine moiety and europium complex of the copolymer is responsible for the conductivity transition in this copolymer device, and Mukherjee and Pal¹⁶ have verified that the charge-transfer complex formation between copper(II) phthalocyanine (CuPc) and fullerenol is accounted for the conductivity transition in their mixed device.

In this letter, a nonvolatile organic WORM memory device with simple structure and construction process was demonstrated based on hexadecafluoro-copper-phthalocyanine (F_{16} CuPc) single layer sandwiched between indium tin oxide (ITO) anode and Al cathode. The ON state of the device at forward bias is attributed to the interfacial dipole layer formation in the ITO/ F_{16} CuPc interface, which increases the hole injection ability from ITO to F_{16} CuPc, while the OFF state is resulted from the destruction of the interfacial dipole layer which forms a high barrier for hole injection.

Devices were fabricated on patterned ITO coated glass substrates with a sheet resistance of 15 Ω /sq. The substrates were routinely cleaned and treated in an ultraviolet (UV)-ozone environment for 10 min before loading into a high vacuum chamber. Organic layers and Al cathode were deposited onto the substrates via thermal evaporation at 5×10^{-4} Pa. Three types of devices were fabricated with the configurations as follows:

Device A: ITO/F₁₆CuPc (80 nm)/Al Device B: ITO/4,7-diphenyl-1,10-phenanthroline (Bphen) (40 nm)/F₁₆CuPc (40 nm)/Al Device C: ITO/F₁₆CuPc (40 nm)/Bphen (40 nm)/Al

Deposition rates and thickness of the layers were monitored *in situ* using oscillating quartz monitors. The evaporating rates were kept at 0.5–1 Å/s for organic layers and 10 Å/s for Al cathode, respectively. Current-voltage (I-V) characteristics of the devices were measured with a Keithley 2400 power supply and were recorded simultaneously with measurements. The forward electric voltage is defined as that the ITO electrode is positive biased. Small angle x-ray diffraction (XRD) patterns were measured with a Rigaku D/Max-2500 diffractometer using Cu K α radiation ($\lambda = 1.54056$ Å). All the measurements were carried out at room temperature under ambient conditions (temperature of ~20 °C and relative humidity of 20%–30%) without encapsulation.

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FIG. 1. I-V curves of the as fabricated device A and that after storage in air for 24 and 48 h.

Figure 1 depicts the I-V curves of the as fabricated device A and that after storage in air for 24 and 48 h. The as fabricated device remains in ON state for the first voltage sweep from 0 to 10V and for the second one from 0 to -4 V. However, with further increase of the reverse voltage from -4 to -10 V, a negative differential resistance (NDR) region appears, indicating that the device switches from the ON state to OFF state. Such a transition is corresponding to the "writing" process of a digital memory cell. After this voltage sweep, the device remains in the OFF state for the latter voltage sweeps in both the positive and negative voltage regions, and it cannot be recovered to the ON state again. The ON/OFF current ratio is obtained by dividing the current density of the ON state by the OFF state. Figure 2 shows the ON/OFF current ratio as a function of the applied voltage of the as fabricated device A at positive voltage region. As can be found in the figure, the maximum ON/OFF current ratio can reach up to 2.3×10^3 at 2.4 V. Meanwhile, storage stability is another key parameter for memory devices. As can be seen from Fig. 1, the device shows little degradation in current density for both the ON state and OFF state, and the device presents WORM memory characters even after 48 h storage in air. Such characters of device A make it beneficial for nonvolatile WORM memory device.

Figure 3 displays the ON and OFF states retention time of device A. Both the ON state and OFF state current den-



FIG. 3. Retention stability of the ON and OFF states of device A under constant bias of 0.5 V.

sities were measured by applying a constant voltage of 0.5 V to the device with a time interval of 1 s. As the number of the measured data points is limited by the soft of our measurement equipment, only the retention time of 1000 s is provided here. It can be found in Fig. 3 that the ON state and OFF state current densities are almost invariable during 1000 s. Besides, the device is stable even after 48 h storage in air as found in Fig. 1. Thus, judging from the current variety trends shown in Fig. 3, a longer retention time of the ON and OFF states could be expected. Such a long retention time is more important for practical applications.

Figure 4 shows the I-V curves of the as fabricated device A with a different voltage sweep sequence. With the first voltage sweeping from 0 to -6 V, a NDR region is also presented in the I-V curve. Similarly, the device switches from the ON state to OFF state after this voltage sweep, and it can not be recovered to the ON state again. Such findings rule out that the ON state and the NDR of device A are correlated to the voltage sweep in the positive region.

The mechanisms of organic WORM memory devices are generally related to the bulk properties of the active organic layers or the interfacial properties of the organic/electrode. To further understand the working mechanisms of device A, two devices with the structures of ITO/Bphen/ F_{16} CuPc/Al (device B) and ITO/ F_{16} CuPc/Bphen/Al (device



FIG. 2. ON/OFF current ratio as a function of the applied voltage of the as fabricated device A at positive voltage region.



FIG. 4. I-V curves of the as fabricated device A with a different voltage sweep sequence.



FIG. 5. I-V curves of devices B and C.

C) were fabricated. Figure 5 shows the I-V curves of devices B and C. No conductivity transition is found in device B during the voltage sweeps. This finding excludes that the conductivity transition of device A is governed by the bulk properties of F16CuPc or the interfacial properties of F₁₆CuPc/Al. Lin et al. have proposed that the conductivity change in CuPc,¹³ poly(N-vinylcarbazole),¹⁷ and pentacene¹⁸ single layer WORM memory devices was attributed to the interfacial dipole layer formation due to the charges trapped in the defect states which were formed by the permeated metal atoms during the deposition of the metal electrodes. However, the behaviors of our WORM devices are distinguished different from those ones. Given that such a mechanism could be applied to our F16CuPc device, the conductivity transition should be found in device B with a Bphen layer sandwiched between ITO and F₁₆CuPc. The vanished conductivity transition in device B indicates that such a mechanism could not be responsible for the conductivity change in the F₁₆CuPc single layer WORM memory device.

As can be found in Fig. 5 that there is an extra NDR region in the I-V curve of device C for the first voltage sweep from 0 to 10 V, and the peak to valley current ratio is lower than device A for the second voltage sweep from 0 to -10 V. After the second voltage sweep, the device is permanently tuned to OFF state. These findings further confirm that the conductivity transition of device A is not related to the interfacial properties of F₁₆CuPc/Al. Combining with the results found in device B, it comes to the conclusion that the conductivity transition of device A is correlated to the ITO/ F₁₆CuPc interface.

Shen *et al.*¹⁹ have demonstrated that a strong chemical reaction between Al and F_{16} CuPc molecules could occur during the evaporation of the Al electrode, which leads to the formation of an insulating (F_{16} CuPc)₃Al layer. Such an insulating layer restricts the injection of electrons from Al to F_{16} CuPc, and the forward current of Au/ F_{16} CuPc/Al is about two orders of magnitude lower than Au/ F_{16} CuPc/Au although the electron injection barrier of F_{16} CuPc/Au (1.1 eV) is much higher than F_{16} CuPc/Al (0.4 eV). The hole and electron injection barriers are 1.2 and 0.3 eV at Au/ F_{16} CuPc compared to 1.1 and 0.4 eV at F_{16} CuPc/Al, respectively. F_{16} CuPc is an n-type material with a high electron

mobility in the order of 10^{-2} cm V⁻¹ s⁻¹ due to significant molecular stacking and π -electron overlap.²⁰ The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of F₁₆CuPc are 6.3 and 4.8 eV, respectively.²¹ In view of almost the same work function of UV-ozone treated ITO and Au,²² a similar high hole injection barrier at ITO/F₁₆CuPc could be expected. Judging from the hole injection barrier at ITO/F₁₆CuPc and low conductivity of the (F₁₆CuPc)₃Al insulating layer, it is difficult for holes to inject from ITO to F₁₆CuPc and for electrons to inject from Al to F₁₆CuPc, which is contravention to the high conductivity found in the forward bias of device A.

To further understand the ITO/F₁₆CuPc interfacial properties, small angle XRD patterns were investigated. Figure 6 reveals the XRD patterns of 20 nm F₁₆CuPc film on quartz and ITO substrates. No discernable structure is found in the quartz/F₁₆CuPc film, indicating that there is no ordered structure existence in the bulk of F16CuPc and in the interface of quartz/F₁₆CuPc. In contrast, a diffraction peak at $2\theta = 1.25^{\circ}$ is found in the ITO/F₁₆CuPc film, suggesting that an ordered structure is formed in the ITO/F₁₆CuPc interface. Wu et al.²³ have demonstrated that such an ordered structure is due to the formation of interfacial dipole layer. Similarly, Di et al.²⁴ have proposed that a dipole layer with the direction orientated from ITO to F16CuPc can be formed in the ITO/F₁₆CuPc interface through electron transfer from ITO to F₁₆CuPc. This dipole layer contributes to the decrease of the energy barrier for hole injection and to the enhancement of the hole injection efficiency. Thus, holes can inject from ITO to F₁₆CuPc efficiently under forward bias and then accumulate in the bulk of F_{16} CuPc due to the electron transporting property of F₁₆CuPc. Subsequently, the accumulated holes form a space electric field which facilitates the injection of electrons from Al to F₁₆CuPc and then recombine with holes in the bulk of F₁₆CuPc. Such a mechanism appropriately interprets the high conductivity of device A for the first voltage sweep from 0 to 10 V. However, only electron can inject into device A under reverse bias due to the high hole injection barrier at F_{16} CuPc/Al, and electrons are the major charges in F₁₆CuPc. The interfacial dipole layer would be broken through the neutralization of the anion constituent of the dipole by the injected electrons when a critical reverse



FIG. 6. Small angle XRD patterns of $20\,\text{nm}$ F₁₆CuPc on quartz and ITO substrates.

bias is applied to the device, which leads to the damage of the F₁₆CuPc conductivity by disrupting the molecular stacking and hence decreases the electron injection ability at the ITO/F₁₆CuPc interface. Thus, the NDR in the second voltage sweep can be attributed to the increase of the electron injection barrier due to the destruction of the interfacial dipole layer at high negative electric field. Besides, the destruction of the interfacial dipole layer is irreversible, which permanently switches the device to the OFF state in both the negative and positive voltage regions. It should be noted that a negative voltage which is high enough must be applied to fully switch the device to its low conductivity state. As shown in Fig. 4, the device is not completely turned to OFF state after the voltage sweep from 0 to -6 V. The OFF state current would decrease gradually if the voltage sweep from 0 to -6 V was repeated for several times and eventually it would reach a constant value (not shown here). These findings further confirm that the NDR in Fig. 1 is a result of the destruction of the interfacial dipole layer. Still, substantial future experimental work is required to understand these phenomena and their mechanisms.

It should be noted that there is another NDR in the positive voltage region of device C. The HOMO and LUMO levels of Bphen are 6.4 and 2.9 eV, respectively.²⁵ Due to the electron transporting property of F16CuPc and the HOMO energy offset between F₁₆CuPc and Bphen, the injected holes would be confined in the bulk of F₁₆CuPc and in the interface of F₁₆CuPc/Bphen. In view of the low electron injection efficiency from Al to Bphen, little electrons could inject into the device and then recombine with holes injected from the anode. As a result, holes would be accumulated in the bulk of F_{16} CuPc and in the interface of F_{16} CuPc/Bphen. Thus, a space field is formed by the accumulated holes and hence restricts further injection of holes. The accumulated holes would neutralize the cation constituent of the dipole and hence break some interfacial dipoles, which is confirmed by the lower ON state current in reverse bias as shown in Fig. 5.

In summary, a simple nonvolatile WORM memory device is demonstrated based on F₁₆CuPc single layer. The device presents an ON/OFF current ratio of 2.3×10^3 with long-term storage stability and long retention time in air. The ON state of the device is attributed to the interfacial dipole layer formation due to the electron transfer from ITO to F₁₆CuPc in the ITO/F₁₆CuPc interface, which reduces the hole injection barrier and hence keeps the device in a high conductivity state. The transition from the ON state to OFF state is resulted from the damage of the interfacial dipole layer by disrupting the molecular stacking of $F_{16}CuPc$, which decreases both the hole and electron injection abilities from ITO to F₁₆CuPc. The present results indicate that such a charge transfer induced interfacial dipole layer formation and destruction mechanism hold the promise for potential applications in next-generation nonvolatile WORM memory devices.

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