

Organic nonvolatile memory by controlling the dynamic copper-ion concentration within organic layer

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(Received 13 January 2004; accepted 27 April 2004; published online 25 May 2004)

Copper (Cu) migration into semiconductor materials like silicon is a well-known and troublesome phenomenon often causing adverse effect on devices. Generally a diffusion barrier layer is added to prevent Cu metallization. We demonstrate an organic nonvolatile memory device by controlling the Cu-ion (Cu^+) concentration within the organic layer. When the Cu^+ concentration is high enough, the device exhibits a high conductive state due to the metallization effect. When the Cu^+ concentration is low, the device displays a low conductance state. These two states differ in their electrical conductivity by more than seven orders of magnitude and can be precisely switched by controlling the Cu^+ concentration through the application of external biases. The retention time of both states can be more than several months, and the device is promising for flash memory application. Discussions about the device operation mechanism are provided. © 2004 American Institute of Physics. [DOI: 10.1063/1.1763222]

Electrical-addressable nonvolatile memory devices have attracted considerable attention in recent years due to their application in information technology. Silicon-based floating-gate memory,¹ with a response time in the submillisecond range, has played an important role in modern electronic devices such as the digital camera. However, there is always a strong demand for an electronic nonvolatile memory device which is cheaper and better. Organic electrical bistable devices (OBD) are promising in this regard. Recently, we demonstrated an organic electrical bistable device, with an organic/metal-nanocluster/organic tri-layer structure sandwiched between two electrodes,^{2–4} which shows nonvolatile memory behavior. Many other methods have also been reported for nonvolatile memory, such as phase change memory,⁵ programmable metallization cell,⁶ nano-crystal memory,⁷ organic memory based on scanning probe microscope,⁸ and organic memory in charge-transfer complex system,⁹ and polystyrene films.¹⁰ In this letter, we report an approach to achieve the nonvolatile memory effect by controlling the Cu^+ ion concentration within the organic layer interposed between two metal electrodes.

The structure of the Cu-induced organic bistable device (Cu-OBD) is shown in the inset of Fig. 1. Cu was selected for the electrodes due to its high diffusion coefficient.¹¹ A buffer layer (~ 4 nm thick) was introduced between the organic layer and one of the electrodes and comprised of dielectric materials such as lithium fluoride (LiF) or aluminum oxide. Materials with low conductivity, good film formability, and stability such as 2-amino-4,5-imidazoledicarbonitrile (AIDCN), tris-8-(hydroxyquinoline) aluminum (Alq_3), and zinc 2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine (ZnPc) were selected for the organic layer.

Vacuum thermal evaporation method was selected for device fabrication. Cu was first deposited on a precleaned

glass substrate (anode) followed by the buffer layer, the organic layer, and the top electrode (cathode) without breaking the vacuum. The substrate was transferred from one shadow mask to another by a moving mechanism manually controlled from outside. The device area (0.25 mm^2) was defined by the overlap of the top and the bottom electrodes. The thickness of the buffer layer and the organic layer was 4 and 100 nm, respectively. During the deposition, the vacuum of the chamber was kept at about 1×10^{-6} Torr. The current-voltage (I - V) measurement was carried out using a HP 4155B semiconductor parameter analyzer.

Figure 1 shows the typical I - V characteristics of a Cu-OBD. When the bias is ramped from 0 to 3.5 V, the current injection is initially very low. At a critical voltage (V_{c1}) of approximately 0.7 V the device switches from the low conductance (OFF) state to a high conductance (ON) state. The device stays in the ON state as the bias is increased until it reaches another critical voltage (V_{c2}) around 2 V, where it reverts to the OFF state. Therefore, the transition from the

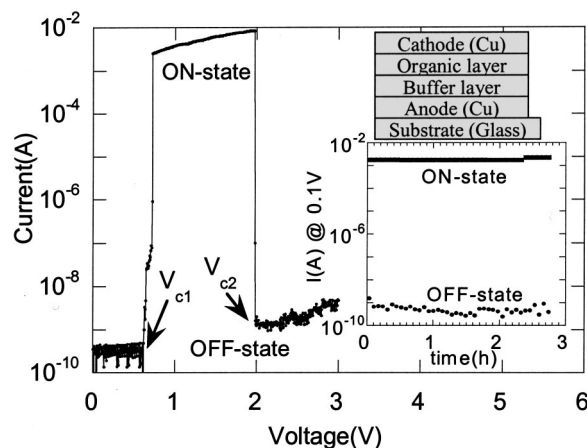


FIG. 1. The typical I - V characteristics of Cu-OBDs. The inset shows the device structure and stress test for device at both ON state and OFF state.

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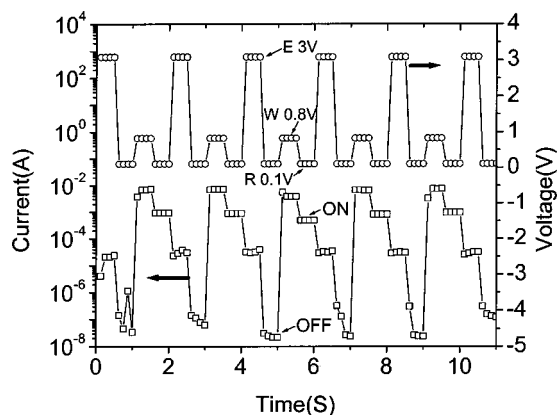
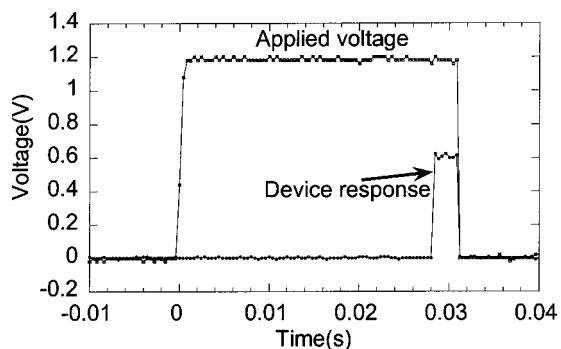
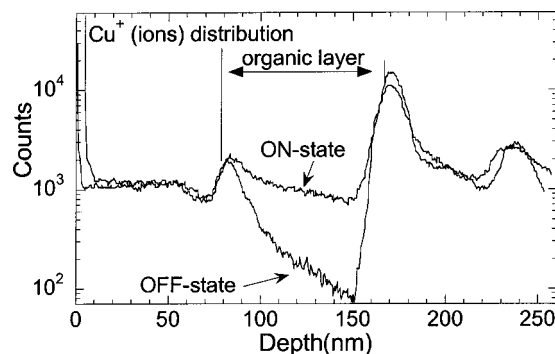


FIG. 2. Write-read-erase cycle test of a Cu-OBD.

OFF state to the ON state (Switch-ON) can be achieved by applying a medium bias ranging from V_{c1} to V_{c2} , and the transition from ON state to OFF state (Switch-OFF) can be achieved by applying a voltage greater than V_{c2} . Interestingly, the Switch-ON and Switch-OFF processes are nonvolatile processes, i.e., once the device switches to either state it remains in that state for a prolonged period of time. A small probing (or reading) bias less than the V_{c1} may be applied to detect the state of the device. Both ON and OFF states are quite stable. The bottom inset of Fig. 1 shows the stress test carried out in the ON and OFF states probed by 0.1 V. We also tested the retention time for both states under no bias condition and found it to exceed 6 months. In addition, we also evaluated the thermal stability of both the states of the Cu-OBDs at 110 °C for several hours in ambient conditions. The device remained in either state without degradation. Therefore, Cu-OBDs can be electrically programmed for rewritable nonvolatile memory applications, as shown in Fig. 2, wherein 0.8 V pulses were used to write, 3 V pulses were used to erase, and 0.1 V pulses were used to read. The current response of the device followed the applied Write-Read-Erase-Read cycles very well.

The dynamic response of our devices to an applied voltage pulse has also been studied to measure the transition speed between the ON and OFF states as shown in Fig. 4, where a 50 Ω read resistor was used to check the device response $\{I(A) = V(V)/50\}$ recorded by a four-channel oscilloscope, Tektronix model TDS-460A (400 MHz). It can be seen from Fig. 3 that when a voltage pulse is applied to the device in the OFF state, it initially remains in the OFF state,

FIG. 3. The transient behavior of a Cu-OBD, where a 50 Ω read resistor was used to record the device response ($I = V/50$).FIG. 4. SIMS Cu^+ depth profile for Cu-OBDs.

but after a delay of about 28 ms it switches to the ON state. However, the Switch-OFF process (data not shown) of the Cu-OBDs is quite fast and takes place in nanoseconds.

It is believed that the ON and OFF states are due to the Cu^+ distribution and subsequent metallization and demetallization. This argument is proved by the secondary ion mass spectrometry (SIMS) depth profile measurement for Cu^+ ion and Cu atom in our devices in both states. It is found that Cu^+ ion was driven into the organic layer in the ON state (metallization process), while Cu^+ drifted out of the organic layer in the OFF state as shown in Fig. 4 (demetallization process). Therefore, the ON-and-OFF state can be switched back and forth by controlling the Cu^+ ion distribution profile within the organic layer. The atomic Cu distribution in the Cu-OBDs (not shown here) was found to be low within the organic layer for both states. Hence the dynamic Cu^+ concentration within the organic layer is responsible for the bistability of Cu-OBDs.

The ON state and OFF state were further investigated by a square wave applied to the device. In Fig. 5, it can be seen that the ON state of the device shows a pure resistor behavior and has a square wave form following the applied voltage pulse. While in the OFF state, the device shows a capacitor behavior and has two peaks that are related to charging and discharging process of the device, respectively. The pure resistor behavior in the ON state and capacitor behavior in the OFF state can also be seen from the device capacitance as

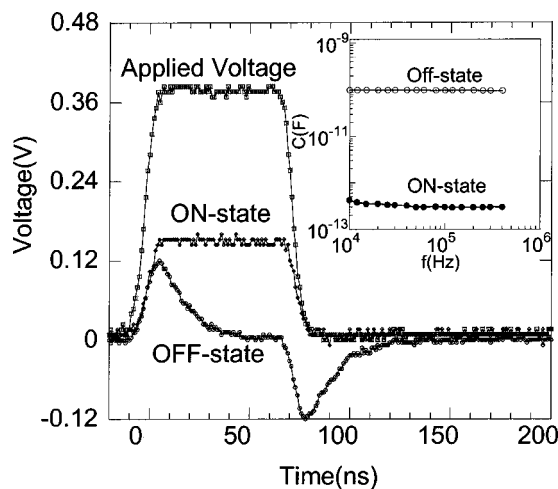


FIG. 5. Transient response for a Cu-OBD at both ON state and OFF state (read mode). Inset: frequency dependence of capacitance of a Cu-OBD at both ON state and OFF states.

shown in the inset of Fig. 5. The ON-state capacitance of the device is very small, less than 1 pF, while the OFF-state capacitance of the device is in the range of 100 pF. Using a parallel-plate capacitor model, the effective thickness of the dielectric layer was estimated to be nearly the same as the thickness of the deposited organic layer. This indicates that copper is not distributed within the organic layer in the OFF state. In the ON state the devices have nearly no capacitance, which suggests that they behave like a resistor, caused by the Cu^+ distributed throughout the organic layer.

Previous studies have indicated that copper diffuses into other materials in a positively charged state,¹² namely Cu^+ ion. The copper ions drift in both silicon¹³ and organic materials,¹⁴ and cause copper metallization. Generally diffusion barrier layers are used to prevent this diffusion/drift and metallization.¹⁵ The diffusion barrier provides interfacial adhesion (or an energy barrier) to prevent Cu^+ diffusion and metallization.¹⁶ For Cu-OBDs, when a positive bias is applied, copper gets ionized at the anode (near the Cu/LiF interface) and the anode acts as a source of Cu^+ ions. Under bias, they drift into the organic layer and towards the cathode. When the Cu^+ ions reach the cathode, a continuous Cu^+ distribution within the organic layer is established, the organic layer is metallized by the Cu^+ and it shows the ON state. This is also consistent with the delay time during the switch-ON process as shown in Fig. 3. The delay time is associated with the traveling time for the Cu^+ ions through the organic layer. One can estimate the drift velocity of Cu^+ in AIDCN film to be about 5×10^{-4} cm/s under an electric field of 1.2×10^5 V/cm, and the diffusivity of Cu^+ in AIDCN film to be about 10^{-10} cm²/s at room temperature. This is smaller than in silicon (about 10^{-7} cm²/s).¹⁷ By selecting organic materials with relatively high Cu^+ ion diffusion coefficients faster switch-ON speed can be expected. When the applied bias exceeds the second critical voltage, V_{c2} , it undergoes a switch-OFF process and the device changes to the OFF state (Fig. 1). The Cu^+ ion injection is interrupted while the residual Cu^+ ions within the organic layer continuously drift toward the cathode where they get reduced to Cu. Once a Cu^+ distribution gap is formed within the organic layer, the device switches OFF. Hence the transition speed from ON to OFF is very fast. The reason for the interruption of Cu^+ ion injection at bias larger than V_{c2} is still unclear, which needs further study.

In summary, we demonstrated a nonvolatile memory device by controlling the copper ion concentration within the organic layer. Devices with the structure of Cu/Buffer-layer/organic/Cu have been fabricated by vacuum thermal deposition method. A small voltage pulse around 0.5 V can switch the device to high conductance state, and a voltage pulse above 2 V can restore it to low conductance state. The two states differ in their conductance in more than seven orders in magnitude, and are quite stable. This opens a promising way for high-performance organic electronic devices.

This research is jointly supported by the Air Force Office of Scientific Research (Program manager Dr. Charles Lee, fund number F49620-03-1-0101) and by Office of Naval Research (Program manager Dr. Paul Armistead, fund number N00014-04-1-0434).

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