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Organic electrical bistable devices and rewritable memory cells

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Electrical bistability is a phenomenon in which a device exhibits two states of different conductivities, at the same applied voltage. We report an organic electrical bistable device (OBD) comprising of a thin metal layer embedded within the organic material, as the active medium [L. P. Ma, J. Liu, and Y. Yang, US Patent Pending, (2001)]. The performance of this device makes it attractive for memory-cell type of applications. The two states of the OBD differ in their conductivity by several orders in magnitude and show remarkable stability, i.e., once the device reaches either state, it tends to remain in that state for a prolonged period of time. More importantly, the high and low conductivity states of an OBD can be precisely controlled by the application of a positive voltage pulse (to write) or a negative voltage pulse (to erase), respectively. One million writing-erasing cycles for the OBD have been tested in ambient conditions without significant device degradation. These discoveries pave the way for newer applications, such as low-cost, large-area, flexible, high-density, electrically addressable data storage devices. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1473234]

Electrical bistability is a phenomenon in which a device exhibits two states of different conductivities, at the same applied voltage. This behavior is ideal for switching and memory applications and has been demonstrated in both inorganic and organic materials.[1–11] In this manuscript, we report an organic bistable device (OBD).[12] The structure of our OBD is fairly simple and consists of an organic/metal/organic, triple-layer structure interposed between an anode and a cathode [Fig. 1(a)]. We selected organic compounds with relatively high dielectric constant and good film-forming characteristics. We discuss the results obtained using 2-amino-4, 5-imidazoledicarbonitrile (AIDCN) as the organic layer, and aluminum (Al), as the embedded metal layer and also the electrode layers. The chemical structure of AIDCN is shown in Fig. 1(b).

The fabrication of OBDs is quite similar to the fabrication of organic light-emitting diodes. Precleaned glass substrates were coated with 800 Å of Al by thermal evaporation. The electrodes on the glass substrate are defined as anodes, which were patterned into parallel columns of width 1 mm by the shadow mask technique. The first organic layer, the middle metal layer, and the second organic layer were sequentially deposited on top of this anode. The device was completed by the deposition of the cathode layer comprising of an ~800-Å-thick Al layer. The cathode was patterned into parallel row electrodes of width 1 mm, by another shadow mask step. The overlap between the column and row electrodes defined the dimensions of the OBD ($1\ \mathrm{mm}^2$). All deposition processes were carried out in a vacuum of 1×10^{-6} Torr in an evaporator equipped with six sources, and all the steps, including mask changeover for the electrode patterning were conducted without breaking the vacuum. The thickness of the metal and organic films was recorded with a quartz crystal monitor and further verified with a Dektak, thin film profilometer and an ellipsomemter. The thickness of each embedded organic layer and the Al layer was about 50 and 20 nm, respectively. Unless specified, all electrical tests were conducted in ambient condition without any device encapsulation. $I-V$ curves were measured using an HP 4155A semiconductor parameter analyzer. The write-read-erase-read cycles were performed using a programmable Keithley 2400 power supply and recorded with a four-channel oscilloscope (Tektronix TDS 460A).

Figure 2 shows typical $I-V$ curves for an AIDCN-based OBD. The first voltage scan depicted by curve (a) shows a sharp increase in the injection current at about 2 V indicating the transition of the device from the low conductivity state (OFF state) to a high conductivity state (ON state). This transition from the OFF state to the ON state is equivalent to the ‘‘writing’’ process in a digital memory cell. The ratio of the conductivities achieved between the two states is about 10^4. After this transition, the device remained in this state even after turning off the power. This can be seen in the

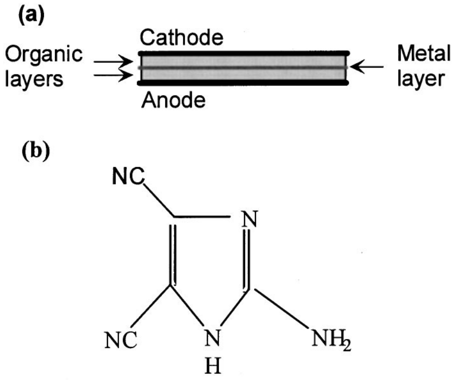

FIG. 1. The structure of an electrical bistable device and the chemical structure of the organic material. (a) The device structure and (b) the chemical structure of AIDCN.

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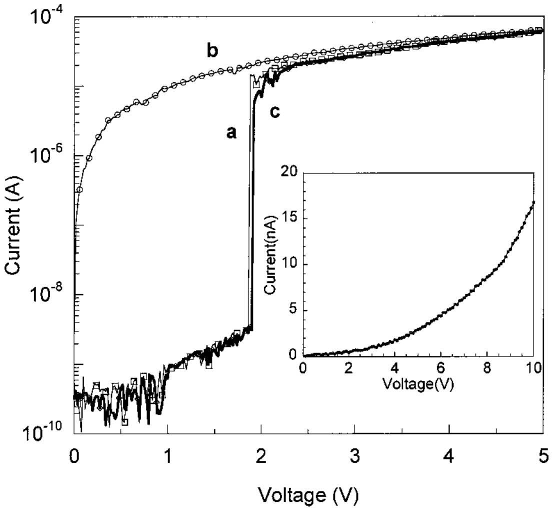

FIG. 2. $I-V$ characteristics of an OBD with the structure Al/AIDCN (50 nm)/Al (20 nm)/AIDCN (50 nm)/Al. Voltage was scanned in steps of 0.1 V from 0 to 5 V. Curves (a) and (b) represent the $I-V$ characteristics of the first and second bias scan respectively. Curve (c) is the $I-V$ curve of the third bias scan after the application of a reverse voltage pulse (-3 V).

second voltage scan [curve (b)] in Fig. 2. The two $I-V$ curves in Fig. 2 define the electrical bistability of the OBD and also reveal the nonvolatile nature of the memory effect. One of the most important features of our OBD is that the OFF state can be recovered by the simple application of a reverse voltage pulse. This is equivalent to the "erasing" process of a digital memory cell. Curve (c) in Fig. 2 shows the $I-V$ characteristics of the device after the application of a -3 V bias; and is nearly identical to curve (a). However, the bistable behavior, the OFF–ON transitions, and the creation of nonvolatile memory effects can be observed only in the presence of the embedded thin metal layer. The inset of Fig. 2 shows the $I-V$ curves of a device using a 50-nm-thick AIDCN layer as the active medium, where these phenomena can no longer be observed. The switching time for the OBD is in the nanoseconds time scale (Fig. 3). The switching time of 10 ns originates from the RC time constant of the measurement system. The actual switching time is likely to be faster than 10 ns.

One of the promising applications of the OBD is the organic rewritable memory, which can be used in personal computers, personal digital assistants, and digital cameras etc. The precise control over the ON–OFF states, multiple rewriting ability, and device stability are the key issues for these applications. More than one million write-erase cycles were conducted on our OBD with good rewritable characteristics as shown in Fig. 4. Although there are some small electrical spikes, the states of the OBD cell follow the pulses acceptably, as indicated by two different currents at the same voltage. It should be noted that the time scale used, as shown in Fig. 4 was due to the inherent limitations of our testing equipment and program.

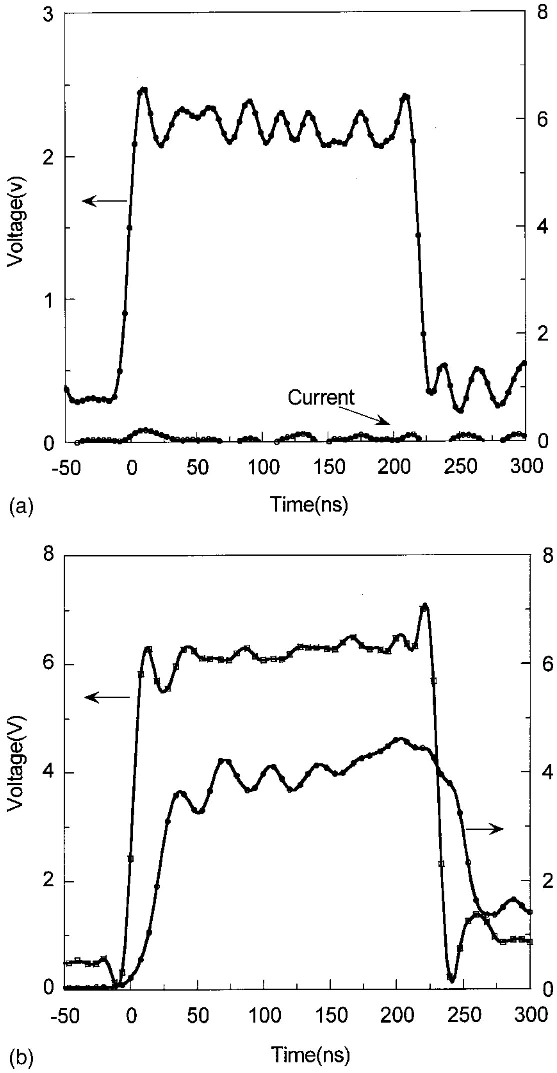

FIG. 3. The transient behavior of an OBD below and above the threshold voltage. (a) The electrical current response of an OBD initially in the OFF state. A voltage pulse less than the switch-on voltage (3 V, in this example) is applied to confirm the low conductivity state of the OBD; (b) the electrical current response of the same OBD under a voltage pulse (6 V) higher than the switch-on voltage for ~10 ns transforms it to the high conductivity state.

In addition to the rewriting capability, the retention of the ON and OFF states and the device performance under stress are important for practical applications. The memory retention ability was tested by leaving several OBDs in the ON state at ambient conditions. It was found that the devices remained in the ON-state for several days to weeks. The origin of the variation in the retention ability is still under investigation. The stability of the OBDs under stress was evaluated in the continuous bias condition. A constant voltage (1 V) was applied to the OBD in the OFF state and the ON state and the current recorded at different times. As can be seen from Fig. 5, there is no significant degradation of devices in both the OFF and ON states after 4-h of continuous stress test, indicative of the stability of both the material and the metal/organic interfaces. The current measured in the OFF state is within the resolution of the Keithley 2400.

Although the mechanism is still under investigation, it is believed that the embedded metal layer plays an important role of establishing the sudden increase of injection current and the retention of high conductivity status after the bias is off. It is suspected that trapped charges in the middle metal layer and dynamic doping process of organic films is responsible for the observed electrical bistability and the nonvolatile memory effect. It should be noted that the detailed mechanism of the electrical bistability of the OBDs needs

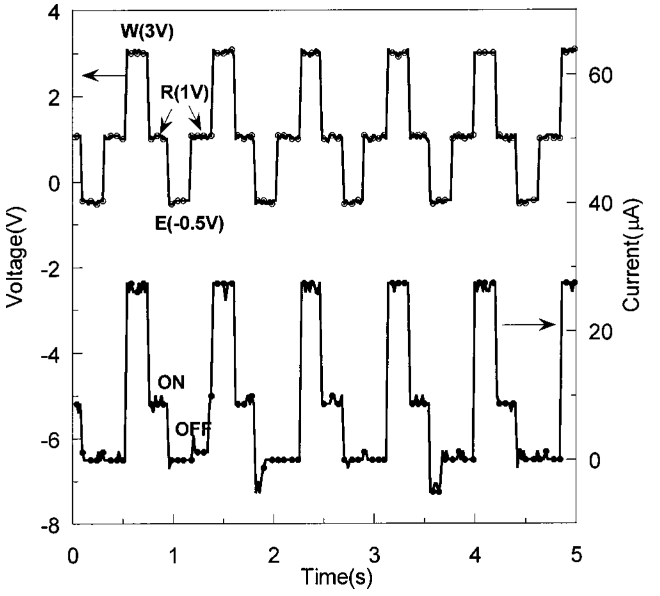

FIG. 4. Typical current responses of an OBD during the write-read-erase-read voltage cycles; the writing voltage pulse (W) is 3 V, the erasing voltage pulse (E) is -0.5 V. In order to confirm the successful registration of the ON and OFF states, a small reading bias (R) of 1 V was applied to the device immediately following the writing and erasing pulses to determine the state of the OBD.

further study and this is an early stage of the investigation of this device.

It is worth to mention here that electrical bistability in organic materials has been studied in the past and been attributed to various mechanisms, such as the change of molecular structures,[4,5] the formation of conducting filaments,[6–8] the formation of charge transfer complexes,[9,10] and two-step reduction processes.[11] The major difference in our OBDs is the presence of the embedded metal layer within the organic films. Initial experimental results indicate that the embedded metal layer plays a critical role in determining the $I-V$ characteristics of the OBDs. Electrical bistability can only be observed when the thickness of this metal layer is greater than a critical value (10 nm). When the layer is too thin or in the absence of the metal layer, the bistability phenomenon disappears and very low current injection is observed. The mechanism of our OBD does not appear to be associated with the formation of conducting filaments, which has caused concerns in the past. If metal filaments were responsible, then the electrical properties of the ON state of our OBD would be expected to be similar to the metal. On the contrary, the conductance of our OBDs decreases with decreasing temperature. The OFF state in the devices with the reported formation of conducting filaments, was achieved independent of the polarity of the applied current pulse.[6,7,9,10] In our OBDs, the OFF (low conductivity) state can be recovered only by applying a reverse voltage pulse. In addition, if the formation of conducting filaments were involved, the injected current would be insensitive to the device area,[7,8] which is again contrary to the observations on our OBD.

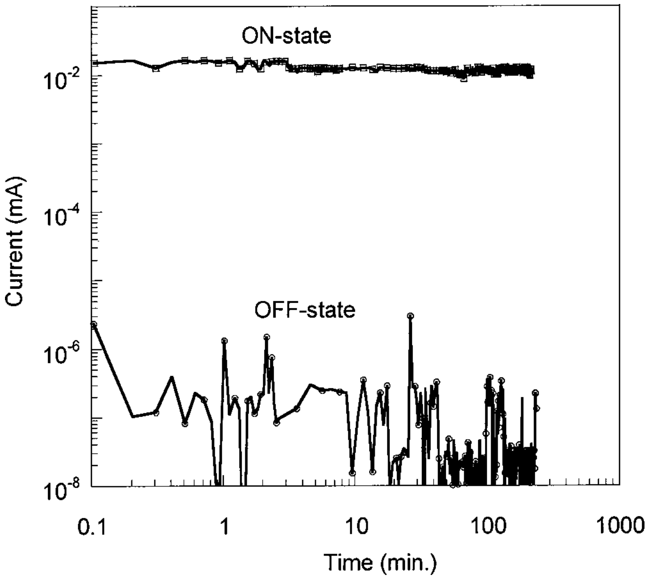

FIG. 5. The stability test of an OBD in either the ON or OFF state under a constant bias (1 V).

In summary, high performance organic electrical bistable devices have been demonstrated with a simple structure, i.e., an organic/metal/organic triple-layer interposed between two electrodes. The OBDs have two distinctive states of conductivity that can be achieved by applying voltage pulses with different polarities. The OBDs remain in either state even after the power is turned off, making them ideal candidates for nonvolatile memory cells. More than a million write and erase cycles were performed on the OBDs in ambient conditions without any device encapsulation. OBDs are significant because of two reasons. First, these devices use organic insulators as the active material. This provides options with respect to materials available for organic electronic devices, which have been traditionally associated with organic semiconductors. Second, OBDs have a tremendous potential for low cost, large-area and high-density memory cells. It is anticipated that the development of this device will have a tremendous impact on the electronic industry.

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