AIP | Applied Physics Letters

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Citation: Appl. Phys. Lett. **93**, 083301 (2008); doi: 10.1063/1.2973902
View online: http://dx.doi.org/10.1063/1.2973902
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v93/i8
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Memory effect and negative differential resistance in tris-(8-hydroxy quinoline) aluminum/bathocuproine bilayer devices

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(Received 10 April 2008; accepted 29 July 2008; published online 26 August 2008)

Memory effect and negative differential resistance (NDR) were observed in simple tris-(8-hydroxyquinoline) aluminum/bathocuproine (BCP) bilayer devices. The devices could be switched from a low conductance state to a high conductance state when a negative bias was applied and could be restored to an OFF state when a positive bias was applied beyond the NDR region. The memory effect is nonvolatile, and an ON/OFF ratio of over 10^3 was achieved. The memory effect was observed only in the presence of both Alq_3 and BCP layers, and the NDR is attributed to the defects formed in the BCP layer upon evaporation of an Al cathode. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2973902]

For the expeditious advancement of information technology, there is a strong need for an electronic memory device that is cheaper, smaller, and high in storage density. Recently, there has been a growing interest to develop organic memory devices because they offer many advantages compared to traditional silicon-based memory devices, such as a simple structure, low fabrication cost, high mechanical flexibility without the need for bulky and expensive mechanical drives used in conventional magnetic and optical memories, easy processing, light weight, electrical bistability, and versatility of an organic chemical structure.[1–15] There are three types of organic memory devices: random access memory, write-once read-many-times memory, and read-write-erasable memory [organic bistable device (OBD)]. The earliest organic memory cell was proposed by Potember and Poehler[16] in the 1970s, where the bistable characteristic is based on the charge transfer between copper and tetracyanoquinodimethane; however, the device was unreliable for a long-term operation. Since then, different configurations have been developed for organic memory devices. These include organic/metal/organic triple-layer devices relying on charge storage in metal nanoparticles,[1–3] gold nanoparticle-polymer composite devices based on charge transfer between gold nanoparticles and organic materials,[4] organic-based donor-acceptor devices via a charge-transfer complex formation,[6,7] and even single-layer devices with a memory behavior due to filament formation[9] or carriers trapped in the defect sites of an organic layer.[10] The development of organic memory devices is still in its early stage, but it is expected to be exciting and rewarding.

Here we report a simple bilayer organic memory device using tris-(8-hydroxy quinoline) aluminum (Alq_3) and bathocuproine (BCP). The device shows remarkable bistability, and the bilayer structure does not require the incorporation of nanoparticles, sandwiched structures, or the precise control of doping concentration and deposition rate. Key parameters that determine the negative differential resistance (NDR) are discussed.

Memory devices were fabricated on patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 30 Ω/sq. The substrates were routinely cleaned and treated in an ultraviolet-ozone environment for 25 min before loading into a high vacuum chamber. Organic layers and an Al cathode were deposited onto the substrates via thermal evaporation at $\sim 10^{-6}$ Torr. Four types of devices were fabricated. Their configurations are as follows:

(1) Device A: ITO/Alq_3 (60 nm)/BCP (20 nm)/Al.
(2) Device B: ITO/2-methyl-9,10-bis(naphthalen-2-yl)-anthracene (MADN) (60 nm)/BCP (20 nm)/Al.
(3) Device C: ITO/bis-(2-methyl-8-quinolinolate)-4-(phenylphenolato)aluminum (BAlq) (60 nm)/BCP (20 nm)/Al.
(4) Device D: ITO/2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) (60 nm)/BCP (20 nm)/Al.

Current-voltage (*I-V*) characteristics of devices A–D are shown in Figs. 1(a)–1(d), respectively. All four devices remained in a low conductance state in the forward bias region [curve (a)]. However, when the voltage was swept from 0 to −10 V [curve (b)], all four devices showed transitions from a low conductivity state (OFF state) to a high conductivity state (ON state), although the ON/OFF transition for device B was less abrupt. This transition is equivalent to the "writing" process in a digital memory cell. The devices remain in the ON state even upon turning off the power, as seen from the voltage scanning from −10 to 0 V in curve (c). This nonvolatile nature is beneficial for OBD. As seen in curve (d), when the voltage was swept from 0 to 10 V, the devices remained in the ON state until the voltage reached approximately beyond 3–4 V. A NDR region appeared as the voltage further increased, representing a transition from the ON state to the OFF state. This ON-OFF transition is equivalent to the "erasing" process in a memory device. The devices remained in the OFF state until a negative bias was reapplied. The ON/OFF ratios of the devices A, B, C, and D are 1.5×10^3, 1×10^3, 1×10^2, and 2×10^2, respectively. It

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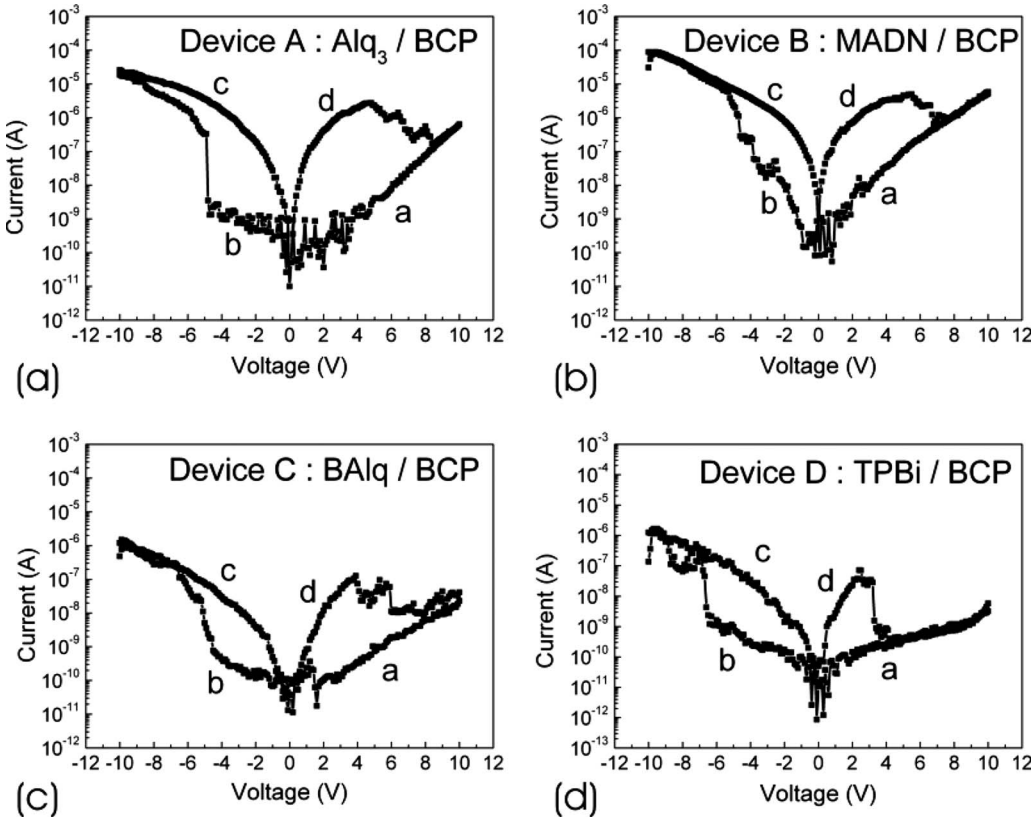

FIG. 1. *I-V* characteristics of (a) ITO/Alq_3 (60 nm)/BCP (20 nm)/Al, (b) ITO/MADN (70 nm)/BCP (10 nm)/Al, (c) ITO/BAlq (60 nm)/BCP (20 nm)/Al, and (d) ITO/TPBi (70 nm)/BCP (10 nm)/Al.

can be seen that the Alq_3/BCP memory device exhibits the highest ON/OFF ratio.

The current response of the Alq_3/BCP device during the write-read-erase-reread cycles is shown in Fig. 2(a). The writing, reading, and erasing voltages are −8, −3, and 8 V, respectively. It was observed that the current changes disciplinarily and reproducibly with the write-read-erase-reread cycle. Figure 2(b) depicts the current retention ability of the Alq_3/BCP memory device after 1000 write-read-erase-reread cycles. Current was recorded at a voltage of −3 V for a reverse scan (OFF state) and a forward scan (ON state). The current for "reading" the memory device at both the ON state and the OFF state is very stable, indicating that the Alq_3/BCP memory device has a good rewriting capability and retention ability.

To understand the mechanism of the organic memory device, a single-layer device with either an 80 nm thick Alq_3 or a BCP layer sandwiched between the ITO and Al electrodes was fabricated. However, neither bistability nor NDR was found (not shown here). It is therefore substantiated that memory effect and permanent NDR can be observed only in the presence of both Alq_3 and BCP.

The NDR in the case of Alq_3/BCP (in total thickness of 100 nm) cannot be explained by a leakage current, by a simple charge transport, or by a carrier injection model. It should be noted that the evaporation temperature of Al is approximately 1300 °C. When an Al cathode was deposited directly onto BCP, the hot metal atoms would create defects in the organic layer[14] due to Al interaction with the lowest unoccupied molecular orbital (LUMO) of BCP.[17] Consequently, the electron traps in the proximity of the cathode formed a space charge layer, which increased the internal

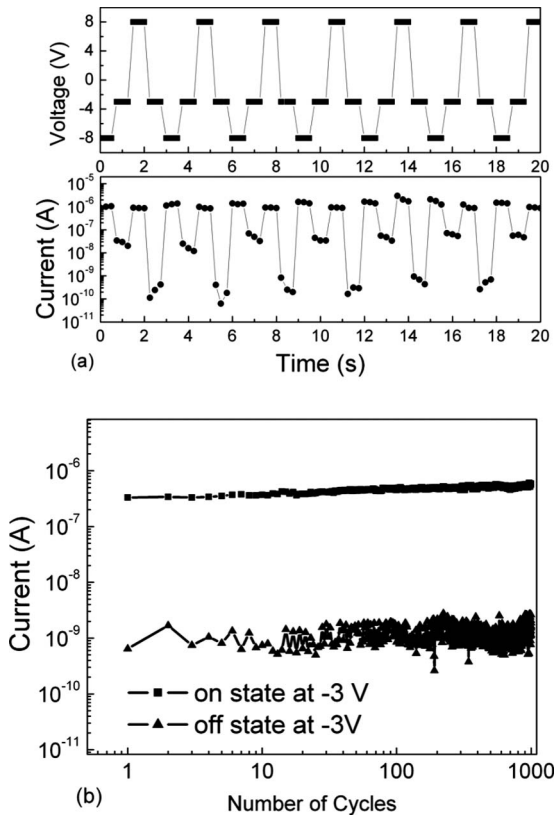

FIG. 2. (a) Current response of the ITO/Alq_3 (60 nm)/BCP (20 nm)/Al device during the write-read-erase-reread voltage cycles. The writing, reading, and erasing voltages are −8, −3, and 8 V, respectively. (b) Current retention ability of the ITO/Alq_3 (60 nm)/BCP (20 nm)/Al device in either ON or OFF state under a constant voltage of −3 V.

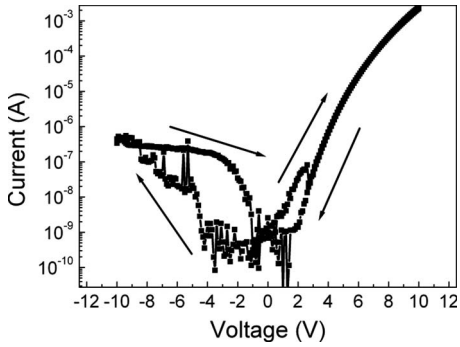

FIG. 3. *I-V* characteristics of the ITO/Alq_3 (60 nm)/BCP (20 nm)/LiF (1 nm)/Al device.

electric field and hence facilitated hole injection from ITO into Alq_3. Nevertheless, at a voltage beyond 4 V in the case of Alq_3/BCP [Fig. 1(a)], the increased electrons trapped in the defect sites drastically decreased the current by two orders of magnitude.

To investigate the effect of defect states on the bistability of the memory device, another device with a thin layer of LiF inserted between the BCP and Al cathode was fabricated. The device structure is device E:ITO/Alq_3 (60 nm)/BCP (20 nm)/LiF (1 nm)/Al. It has been reported that the inserted LiF layer can suppress the chemical reaction between the organic material and the Al cathode and hence reduce the density of the defect sites.[15,18] The *I-V* characteristics of device E is shown in Fig. 3. A similar bistability was observed in the negative voltage region, but strikingly the NDR in the positive voltage region disappeared. Instead, the current increased by several orders of magnitude when the voltage swept to 10 V. The prominent increase in current in the positive bias region should be attributed to the improved injection of electrons due to the inserted LiF layer. The result substantiates that the defect states formed upon Al evaporation onto the BCP layer play a significant role in determining the NDR but do not influence the ON/OFF ratio of the present bilayer memory device.

So far it has been shown that the devices do not exhibit a memory effect if we do not deposit an organic layer underneath the BCP. Also, different organic materials used for the first layer (OL1) of the bilayer memory device would lead to different ON/OFF ratios. Therefore, the interface formation between the ITO and OL1 or between the OL1 and BCP could be of particular importance to account for the operation mechanism of the bilayer memory cell. BCP is a well-known hole blocking layer with HOMO and LUMO levels of 6.5 and 3.0 eV, respectively. It is anticipated that OL1 with an appropriate energy level that matches with that of the ITO and BCP could facilitate an abrupt increase in current flow beyond a particular threshold voltage. Factors that govern the ON/OFF ratio in the bilayer device are under further investigation.

In summary, bistability and NDR were observed in the Alq_3/BCP, MADN/BCP, BAlq/BCP, and TPBi/BCP bilayer devices. The memory device consisting of Alq_3/BCP exhibits the highest ON/OFF current ratio of 1500. The current for writing and reading the memory device is very stable, leading to desirable rewriting capability and retention ability. The NDR disappears when a thin layer of LiF is inserted between the BCP and Al. This suggests that the NDR is attributed to the formation of defect states upon evaporation of hot metal atoms onto the BCP layer. Our results show that the simple Alq_3/BCP bilayer device has promising potential for nonvolatile, high-density, and low-cost memory application.

This work was supported by CityU Strategic Research (Grant No. 7001986).

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