Reproducible resistive switching in nonvolatile organic memories

Frank Verbakel, Stefan C. J. Meskers, René A. J. Janssen, Henrique L. Gomes, Michael Cölle, Michael Büchel, and Dago M. de Leeuw

---

Articles you may be interested in

Sub-band transport mechanism and switching properties for resistive switching nonvolatile memories with structure of silver/aluminum oxide/p-type silicon
Appl. Phys. Lett. **106**, 063506 (2015); 10.1063/1.4908540

Forming free resistive switching in graphene oxide thin film for thermally stable nonvolatile memory applications
J. Appl. Phys. **114**, 124508 (2013); 10.1063/1.4823734

Mechanism of resistive switching in Cu/AlOx/W nonvolatile memory structures
J. Appl. Phys. **113**, 164506 (2013); 10.1063/1.4803062

Bipolar resistive switching in Cu/AlN/Pt nonvolatile memory device
Appl. Phys. Lett. **97**, 083502 (2010); 10.1063/1.3483158

Polyheteroarylene films with intrinsic switching mechanism for nonvolatile memory applications
Appl. Phys. Lett. **92**, 193302 (2008); 10.1063/1.2912348

Reproducible resistive switching in nonvolatile organic memories

Frank Verbakel, Stefan C. J. Meskers,[a] and René A. J. Janssen
Molecular Materials and Nanosystems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands and Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands

Henrique L. Gomes
Centre of Electronic Optoelectronics and Telecommunications (CEOT), Universidade do Algarve, Campus de Gambelas, 8000 Faro, Portugal

Michael Cölle, Michael Büchel, and Dago M. de Leeuw
Philips Research Laboratories, High Tech Campus 4 WAG 11, 5656 AE Eindhoven, The Netherlands

Resistive switching in nonvolatile, two terminal organic memories can be due to the presence of a native oxide layer at an aluminum electrode. Reproducible solid state memories can be realized by deliberately adding a thin sputtered Al_2O_3 layer to nominal electron-only, hole-only, and bipolar organic diodes. Before memory operation, the devices have to be formed at an electric field of 10^9 V/m, corresponding to soft breakdown of Al_2O_3. After forming, the structures show pronounced negative differential resistance and the local maximum in the current scales with the thickness of the oxide layer. The polymer acts as a current limiting series resistance. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2806275]

Nonvolatile organic memories consist of *any* organic semiconductor sandwiched between two electrodes, one of which typically is aluminum.[1–6] First, by applying a high bias, the rectifying diode with an aluminum electrode is transformed into a nonlinear resistor that, moreover, often shows a negative differential resistance (NDR).[7] This forming process, however, is not always observed for the devices with a native oxide. The formed memory can be switched between high and low resistance states by applying voltage pulses of different biases but of the same polarity. We have recently shown that the conduction is through filaments and that the switching occurs in the native aluminum oxide.[8] Studies using an Al_2O_3 layer obtained via deliberate oxidation of an aluminum layer support the view of the oxide being the active layer.[9,10]

We note that the yield of working devices is often low and that the forming and switching bias voltages are irreproducible.[11] To improve the reliability, we have deliberately added an Al_2O_3 layer with controlled thickness. We show that reproducible memories can then be obtained not only for nominal electron only (*e*-only), but also for nominal hole only (*h*-only), and nominal bipolar diodes. Furthermore, the forming and switching biases systematically vary with the thickness of the Al_2O_3 layer.

The *e*-only diodes consisted of an Al bottom electrode, a sputtered Al_2O_3 layer, a spirofluorene polymer, and a Ba/Al top electrode. For *h*-only diodes the spirofluorene derivate was sandwiched between an indium tin oxide (ITO)/Al_2O_3 bottom electrode and a Pd top electrode. Bipolar diodes were made using an ITO/Al_2O_3 bottom electrode and a Ba/Al electrode. The layout and schematic flatband diagram are presented in the inset of Fig. 3. The devices with an active area of 9 mm^2 were encapsulated to exclude O_2 and H_2O. In all cases, positive bias voltage refers to the bottom electrode being charged positive with respect to the top electrode.

As a typical example, the electrical transport of a pristine *e*-only diode with a 20 nm Al_2O_3 layer is presented in Fig. 1. Figure 1(a) shows cyclic *J-V* scans indicated by arrows where the maximum bias is increased stepwise. In the first scan, the current density increases with bias up to 10^{-4} mA/cm^2 at 2 V. Strong hysteresis is observed; the cur-
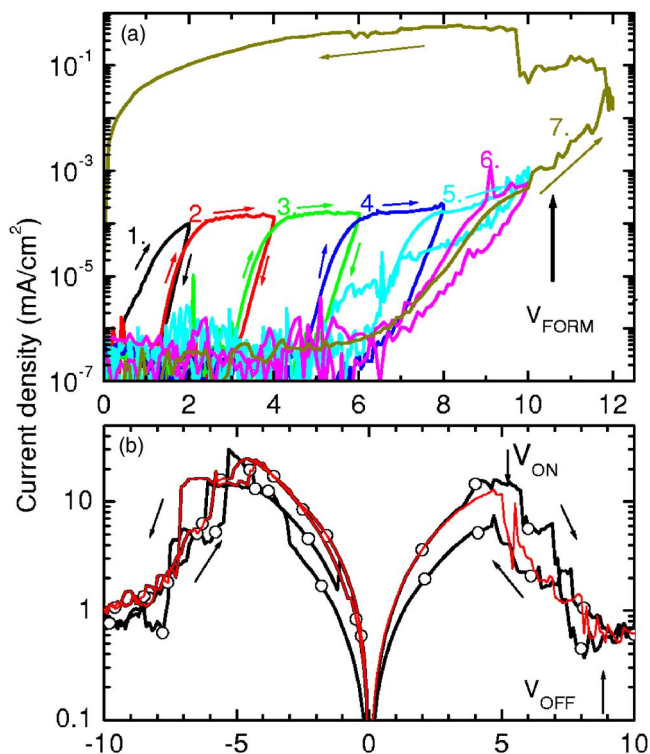

FIG. 1. (Color online) (a) Sequential *J-V* characteristic of a nominal *e*-only diode with an additional 20 nm Al_2O_3 layer (Al/Al_2O_3/polymer/Ba, Al). The maximum applied bias voltage is increased in steps. v_{form} is the voltage required for the forming process. (b) The device after forming [first scan (–○–), second scan (—)] showing the NDR, with V_{on} and V_{off} as the voltage used for switching. The scan speed of the *J-V* characterization is 1 V/s.

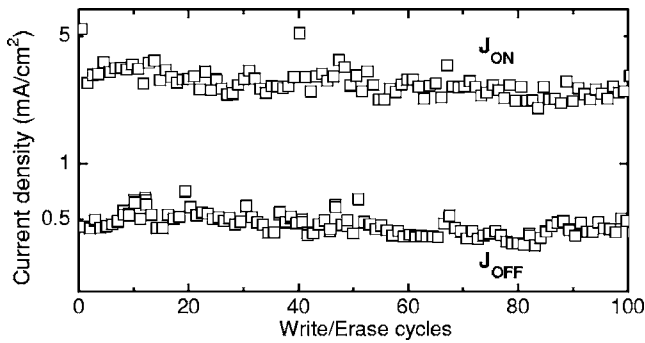[a]Electronic mail: s.c.j.meskers@tue.nl

FIG. 2. The current density under application of the +0.5 V read pulses after a +5 V write pulse (J_{on}) or a +10 V erase pulse (J_{off}), both with a length of 100 ms.
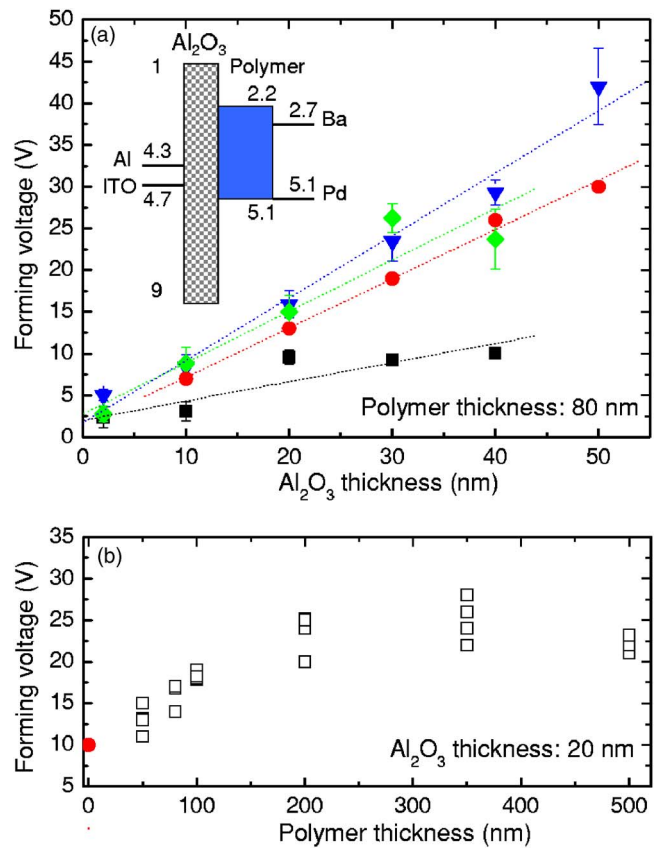

FIG. 3. (Color online) (Inset) Flatband diagram for the diodes (eV). (a) Forming voltage vs the layer thickness of Al_2O_3 (polymer thickness: 80 nm). (Al/Al_2O_3/polymer/Ba,Al) (▼), (ITO/Al_2O_3/polymer/Pd) (■), (ITO/Al_2O_3/polymer/Ba,Al) (♦), and (Ti/Al_2O_3/Al) (●) device structures. (b) Forming voltage vs the polymer layer thickness (Al_2O_3 thickness: 20 nm) (Al/Al_2O_3/polymer/Ba,Al) (□) and without polymer (Ti/Al_2O_3/Al) (●).

rent density scanning back is negligibly low. In the subsequent scans, the current density sharply increases at about the maximum bias of the previous scan. This *J-V* behavior is typical for charge trapping. It seems still reversible, albeit on a time scale of hours.

At about 10 V, the forming voltage, a sudden increase in current density is observed. Figure 1(b) shows that the *J-V* characteristics have irreversibly changed into that of a symmetric but nonlinear resistor with a pronounced NDR. Typically, at biases above the maximum of the NDR, the *J-V* traces show large current fluctuations.

After forming, the devices can be switched reversibly between a high and a low resistance state. Figure 2 shows the current density of the read voltage pulse upon applying 100 sequential write/read/erase/read voltage pulses. Reliable switching is obtained when the biases correspond to the NDR.[12,13] At the voltage corresponding to onset of the NDR, where the current reaches a maximum [here +5 V (or −5 V)], the memory switches to the low resistance state, while at the minimum current, at the end of the NDR [here +10 V (or −10 V)], the high resistance state is obtained. The on/off ratio is typically one order of magnitude. In this experiment, a minimum pulse width of 10 ms is necessary to induce resistive switching. The higher the pulse width, the better is the switching reliability; usually a pulse width of 100 ms gives a switching reproducibility of almost 100%.

We systematically varied the thickness of the Al_2O_3 layer. The polymer layer was fixed at 80 nm. Figure 3(a) shows that the forming voltage for *e*-only diodes (▼) increases linearly with Al_2O_3 thickness. For comparison, we included breakdown voltages reported for Ti/Al_2O_3/Al diodes (●). The good agreement indicates that the forming field of the organic memories is similar to the reported soft breakdown field of Al_2O_3, viz., about 10^9 V/m.[14,15] For a fixed thickness of the Al_2O_3 layer of 20 nm, we varied the thickness of the polymer film. Figure 3(b) shows the forming voltage as a function of the layer thickness. Up to about 200 nm, a linear dependence is observed indicating that the equivalent circuit is a simple series resistance of a polymer and Al_2O_3 layer. The deviation for thicker polymer layers is not yet understood.

Switching is not limited to *e*-only diodes. By adding Al_2O_3 layers to the stack, we realized memories from *h*-only and bipolar diodes as well. The forming voltages as a function of Al_2O_3 thickness are presented in Fig. 3(a). Similar as for the *e*-only diodes, a linear dependence is obtained. The forming field for the bipolar diodes is similar to that of the

e-only diodes. For the *h*-only diodes, the field is smaller by about a factor of 2. Although the difference might be related to limited injection by the Pd electrode, it is not yet fully understood. For all memories investigated, the optimal switching biases, V_{on} and V_{off}, correspond to the maxima and minima in the NDR. The switching biases, presented in Table I, systematically increase with Al_2O_3 layer thickness, for V_{on} to 10 V and for V_{off} to 20 V. For all memories, the current density was measured in the on and off states. The current ratios using switching pulses of 100 ms are presented in Table I. The modulation decreases with increasing Al_2O_3 layer thickness. This dependence is counterintuitive and requires further investigation as a function of, e.g., pulse length. The maximum currents observed in the *J-V* characteristics show no correlation with the thickness of the Al_2O_3 or the polymer layer, or with the electrodes, i.e., *e*-only, *h*-only, or bipolar. This can be expected for a filamentary conduction mechanism. We note, however, that the reliability of the switching generally decreases for thicker Al_2O_3 layers.

In order to determine the reproducibility, we fabricated for *e*-only, *h*-only, and bipolar pristine diodes with six different Al_2O_3 layer thicknesses ranging from 2 nm up to 50 nm. Altogether, the forming process was found to occur in 100 out of 100 devices with Al_2O_3. Switching in 50 devices with Al_2O_3 has been investigated and 50 of these show switching, while with only a native oxide layer, the yield is low, a few percent at most. The yield of switching in these memories is

TABLE I. Switching biases, V_{on} and V_{off}, resistance modulation R_{on}/R_{off}, and yield of switching in the memory devices for e-only, h-only, and bipolar pristine diodes as a function of Al_2O_3 layer thickness, with the number of switching events in the total number of write/erase cycles performed in parentheses.

Al_2O_3 (nm)	V_{on}	V_{off}	R_{on}/R_{off}	Yield (%)	
e-only: $Al/Al_2O_3/polymer/Ba,Al$					
2	⋯	⋯	⋯	~0	(0/7)
10	4	8	~100	~90	(24/27)
20	5	10	~10	~100	(15/15)
30	10	20	~5	~100	(30/30)
40	10	20	~5	~100	(30/30)
50	10	20	~4	~100	(30/30)
h-only: $ITO/Al_2O_3/polymer/Pd$					
0	⋯	⋯	⋯	~0	(0/9)
2	2.5	5	~100	~50	(9/17)
10	3	6	~50	~90	(23/25)
20	5	10	~2	~100	(11/11)
30	5	10	~2	~100	(10/10)
40	5	10	~5	~90	(8/9)
bipolar: $ITO/Al_2O_3/polymer/Ba,Al$					
0	2.5	5	~10	~15	(3/19)
2	2	5	~4	~80	(14/18)
10	4	8	~2	~90	(32/35)
20	6	12	~50	~85	(21/25)
30	6	12	~2	~100	(25/25)
40	8	16	~2	~90	(18/20)

presented in Table I. The reproducibility increases to about unity when an Al_2O_3 layer is inserted in the stack. It clearly demonstrates that a native aluminum oxide layer, which can be present when using Al electrodes, can cause resistive switching effects. The organic semiconductor only acts as a current limiting series resistance.

[1] J. C. Scott and L. D. Bozano, Adv. Mater. (Weinheim, Ger.) **19**, 1452 (2007).
[2] L. Ma, S. Pyo, J. Ouyang, Q. Xu, and Y. Yang, Appl. Phys. Lett. **82**, 1419 (2003).
[3] L. D. Bozano, B. W. Kean, M. Beinhoff, K. R. Carter, P. M. Rice, and J. C. Scott, Adv. Funct. Mater. **15**, 1933 (2005).
[4] P. D. Hooper, G. McHale, and M. I. Newton, Int. J. Electron. **81**, 435 (1996).
[5] V. A. Kolesnikov, V. I. Zolotarevsky, and A. V. Vannikov, Phys. Status Solidi A **200**, 388 (2003).
[6] S. Berleb, W. Brütting, and M. Schwoerer, Synth. Met. **102**, 1034 (1999).
[7] G. Dearnaley, A. M. Stoneham, and D. V. Morgan, Rep. Prog. Phys. **33**, 1129 (1970).
[8] M. Cölle, M. Büchel, and D. M. de Leeuw, Org. Electron. **7**, 305 (2006).
[9] A. Prakash, J. Ouyang, J.-L. Lin, and Y. Yang, J. Appl. Phys. **100**, 054309 (2006).
[10] C. W. Chu, J. Ouyang, J.-L. Lin, and Y. Yang, Adv. Mater. (Weinheim, Ger.) **17**, 1440 (2005).
[11] W.-J. Joo, T.-L. Choi, J. Lee, S. K. Lee, M.-S. Jung, N. Kim, and J. M. Kim, J. Phys. Chem. B **110**, 23812 (2006).
[12] L. D. Bozano, B. W. Kean, V. R. Deline, J. R. Salem, and J. C. Scotta, Appl. Phys. Lett. **84**, 607 (2004).
[13] J. G. Simmons and R. R. Verderber, Proc. R. Soc. London, Ser. A **301**, 77 (1967).
[14] W.-T. Li, D. R. McKenzie, W. D. McFall, Q.-C. Zhang, and W. Wiszniewski, Solid-State Electron. **44**, 1557 (2000).
[15] J. Lee, S. S. Kim, and S. Im, J. Vac. Sci. Technol. B **21**, 953 (2003).