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Citation for published version (APA):<br>Verbakel, F., Meskers, S. C. J., Janssen, R. A. J., Gomes, H. L., Cölle, M., Büchel, M., \& Leeuw, de, D. M. (2007). Reproducible resistive switching in nonvolatile organic memories. Applied Physics Letters, 91(19), 192103-1/3. [192103]. https://doi.org/10.1063/1.2806275

## DOI:

10.1063/1.2806275

## Document status and date:

Published: 01/01/2007

## Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

## Please check the document version of this publication:

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# Reproducible resistive switching in nonvolatile organic memories 

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(Received 6 July 2007; accepted 17 October 2007; published online 7 November 2007)
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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 $10^{9} \mathrm{~V} / \mathrm{m}$, corresponding to soft breakdown of $\mathrm{Al}_{2} \mathrm{O}_{3}$. 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ layer.

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

[^0]As a typical example, the electrical transport of a pristine $e$-only diode with a $20 \mathrm{~nm} \mathrm{Al}_{2} \mathrm{O}_{3}$ 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 $10^{-4} \mathrm{~mA} / \mathrm{cm}^{2}$ 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 $20 \mathrm{~nm} \mathrm{Al}_{2} \mathrm{O}_{3}$ layer $\left(\mathrm{Al} / \mathrm{Al}_{2} \mathrm{O}_{3} /\right.$ polymer/ $\left.\mathrm{Ba}, \mathrm{Al}\right)$. The maximum applied bias voltage is increased in steps. $v_{\text {form }}$ is the voltage required for the forming process. (b) The device after forming [first scan $(-\bigcirc-)$, second scan (-)] showing the NDR, with $V_{\text {on }}$ and $V_{\text {off }}$ as the voltage used for switching. The scan speed of the $J-V$ characterization is $1 \mathrm{~V} / \mathrm{s}$.


FIG. 2. The current density under application of the +0.5 V read pulses after a +5 V write pulse $\left(J_{\text {on }}\right)$ or a +10 V erase pulse $\left(J_{\text {off }}\right)$, both with a length of 100 ms .
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 $-5 \mathrm{~V})]$, the memory switches to the low resistance state, while at the minimum current, at the end of the NDR [here $+10 \mathrm{~V}($ or $-10 \mathrm{~V})$ ], 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ layer. The polymer layer was fixed at 80 nm . Figure 3(a) shows that the forming voltage for $e$-only diodes ( $\boldsymbol{\nabla}$ ) increases linearly with $\mathrm{Al}_{2} \mathrm{O}_{3}$ thickness. For comparison, we included breakdown voltages reported for $\mathrm{Ti} / \mathrm{Al}_{2} \mathrm{O}_{3} / \mathrm{Al}$ diodes $(\bigcirc)$. The good agreement indicates that the forming field of the organic memories is similar to the reported soft breakdown field of $\mathrm{Al}_{2} \mathrm{O}_{3}$, viz., about $10^{9} \mathrm{~V} / \mathrm{m}$. ${ }^{14,15}$ For a fixed thickness of the $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ layer. The deviation for thicker polymer layers is not yet understood.

Switching is not limited to e-only diodes. By adding $\mathrm{Al}_{2} \mathrm{O}_{3}$ layers to the stack, we realized memories from $h$-only and bipolar diodes as well. The forming voltages as a function of $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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


FIG. 3. (Color online) (Inset) Flatband diagram for the diodes (eV). (a) Forming voltage vs the layer thickness of $\mathrm{Al}_{2} \mathrm{O}_{3}$ (polymer thickness: $80 \mathrm{~nm})$. $\left(\mathrm{Al} / \mathrm{Al}_{2} \mathrm{O}_{3} /\right.$ polymer $\left./ \mathrm{Ba}, \mathrm{Al}\right)(\boldsymbol{\nabla}),\left(\mathrm{ITO} / \mathrm{Al}_{2} \mathrm{O}_{3} /\right.$ polymer $\left./ \mathrm{Pd}\right)(\boldsymbol{\square})$, (ITO/ $\mathrm{Al}_{2} \mathrm{O}_{3} /$ polymer/ $\left.\mathrm{Ba}, \mathrm{Al}\right)()$, and $\left(\mathrm{Ti} / \mathrm{Al}_{2} \mathrm{O}_{3} / \mathrm{Al}\right)(\mathrm{)}$ device structures. (b) Forming voltage vs the polymer layer thickness $\left(\mathrm{Al}_{2} \mathrm{O}_{3}\right.$ thickness: $20 \mathrm{~nm})\left(\mathrm{Al} / \mathrm{Al}_{2} \mathrm{O}_{3} /\right.$ polymer/ $\mathrm{Ba}, \mathrm{Al)}$ ( $\left.\square\right)$ and without polymer $\left(\mathrm{Ti} / \mathrm{Al}_{2} \mathrm{O}_{3} / \mathrm{Al}\right)(\bigcirc)$.
$e$-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, $V_{\text {on }}$ and $V_{\text {off }}$, correspond to the maxima and minima in the NDR. The switching biases, presented in Table I, systematically increase with $\mathrm{Al}_{2} \mathrm{O}_{3}$ layer thickness, for $V_{\text {on }}$ to 10 V and for $V_{\text {off }}$ 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ layers.

In order to determine the reproducibility, we fabricated for $e$-only, $h$-only, and bipolar pristine diodes with six different $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$. Switching in 50 devices with $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 Downloaded 21 Jul 2008 to 131.155.151.25. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

TABLE I. Switching biases, $V_{\text {on }}$ and $V_{\text {off }}$, resistance modulation $R_{\text {on }} / R_{\text {off }}$, and yield of switching in the memory devices for $e$-only, $h$-only, and bipolar pristine diodes as a function of $\mathrm{Al}_{2} \mathrm{O}_{3}$ layer thickness, with the number of switching events in the total number of write/erase cycles performed in parentheses.

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

presented in Table I. The reproducibility increases to about unity when an $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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.

We would like to thank Ton van den Biggelaar for preparing the devices. This research was funded by the Dutch Polymer Institute (DPI), Project DPI No. 523. We also gratefully acknowledge the financial support received from the EC (project PolyApply IST-IP-507143) and Fundação para a Ciência e Tecnologia, research unit 631, CEOT.
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