

Programmable Conductance Switching and Negative Differential Resistance in Nanoscale Organic Films

Troy Graves-Abe and J.C. Sturm
Department of Electrical Engineering
Princeton Institute for the Science and Technology of Materials
Princeton University
Princeton, NJ 08544, U.S.A.

ABSTRACT

Thin (12-nm) self-assembled films of the insulating molecule 11-mercaptoundecanoic acid (MUA) were contacted by gold electrodes in a sandwich structure. Current-voltage scans of the resulting devices revealed symmetric negative differential resistance (NDR) with peaks at ± 3 V and large peak current densities of up to 10^4 A/cm². Devices could be programmed reversibly into nonvolatile high- and low-conductance states by applying 1-ms voltage pulses of 4 V and 10 V, respectively; this conductance could be probed non-destructively with voltages below 2.5 V. A conductance ratio of 10^3 between the high- and low-conductance states was measured. The NDR is attributed to the dynamic alteration of the device conductivity as the voltage is scanned. Devices fabricated with one gold and one aluminum electrode displayed NDR only for positive bias on the gold electrode, which supports a model in which the observed programming and NDR is due to the movement of gold in the film leading to the formation and destruction of conductive pathways through the insulating layer.

INTRODUCTION

The demand for increasingly sophisticated mobile electronic devices has led to great interest in new forms of nonvolatile electronic memory to overcome the performance limitations of the dominant CMOS-based memory technologies [1,2]. Recently, a number of memory technologies based on organic compounds have been demonstrated [3]. Organic devices have several features, including low fabrication costs and material properties that can be tailored to meet specific requirements, that make them attractive candidates for next-generation memory arrays. In this work, we report on novel organic devices that display negative differential resistance (NDR) and programmable, non-volatile conductance switching with characteristics that are promising for potential memory application. The devices consist of a thin (12-nm) film of the insulating molecule 11-mercaptoundecanoic acid (MUA) sandwiched between metal electrodes. The relationship between the NDR and a related programmable conductance switching was investigated with pulsed and low-frequency current-voltage measurements. We also present current-voltage measurements on devices made with different electrode metals.

EXPERIMENTAL DETAILS

Devices were fabricated by depositing a thin film of gold onto a silicon substrate by thermal evaporation (with a 5-nm titanium layer for adhesion). Multiple self-assembled layers of 11-mercaptoundecanoic acid (MUA) (purchased from Aldrich) were grown on the gold film by alternate immersions in millimolar ethanol solutions of MUA and Cu(ClO₄)₂ (purchased from

Aldrich), resulting in repeated bi-layers of MUA and copper [4,5]. Following the growth of 7-8 layers of MUA (total thickness 11-13 nm), a layer of silicon oxide (SiO_x) (70 nm) was deposited by electron-beam evaporation. A shadow mask was used to pattern the deposited layer and prevent damage to the organic layer (due to secondary electrons [6]) in regions that were not covered by oxide. The possible effects of inadvertent exposure of the MUA to secondary electrons (for example, at the edge of the shadow mask) are not known. A second metal layer was then deposited on the MUA by thermal evaporation through a shadow mask. The second metal layer was typically gold (30 nm), although some devices were fabricated with aluminum (30 nm) for comparison. The resulting devices had active areas (defined by regions where the two metal layers overlapped with no SiO_x present) of 50 to 300 μm^2 (Fig. 1). Electrical contact was made to the metal electrodes by probing contact pads on top of the SiO_x layer or adjacent to the device area.

An arbitrary waveform generator was used in high-speed current-voltage scans and to apply voltage pulse sequences to program and read the device. An oscilloscope recorded the resulting current by measuring the voltage across a small resistor (typically 10-100 ohms) in series with device. Low-speed current-voltage scans were conducted with an Agilent 4155C Semiconductor Parameter Analyzer. All measurements were performed in a nitrogen glovebox at room temperature.

DISCUSSION

Low-speed (2 V/s) current-voltage scans on devices with gold top and bottom electrodes revealed symmetric NDR with peaks near ± 3 V (Fig. 2). Peak-to-valley ratios of 5:1 were typical, although ratios as large as 140:1 were measured. Very large peak current densities as high as 10^4 A/cm² were observed. In most cases, devices were initially insulating and it was necessary to scan the voltage from 0 to 8 V several times before NDR characteristics were observed. The peak current could vary by as much as 50% from scan-to-scan, but the NDR was otherwise reproducible. If the devices were measured at higher scan speeds (2×10^3 V/s), the

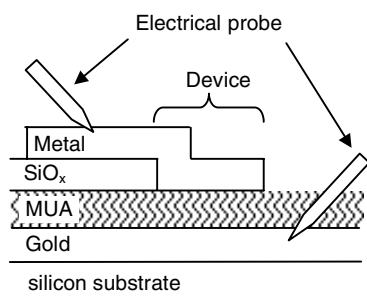


Figure 1. Schematic of device structure. The active device area (defined as regions of metal overlap without the SiO_x layer) is typically 50-300 μm^2 . Electrical contact to the device is made by contacting the metal (gold or aluminum) on top of the SiO_x layer and the bottom gold layer adjacent to the device.

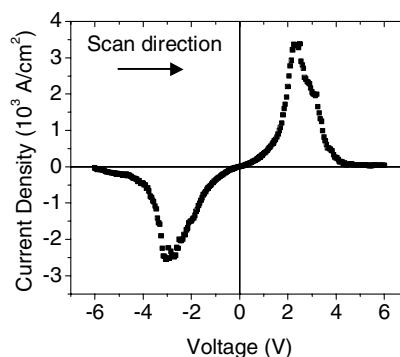


Figure 2. Current density vs applied voltage for a device with gold top and bottom electrodes.

NDR was replaced by a low-conductivity current-voltage characteristic (Fig. 3). The absence of NDR at high frequencies indicates that the NDR is not due to resonant tunneling, a common source of NDR.

To probe the mechanism responsible for NDR, short (1-ms) voltage pulses were applied and then the device conductance at 1 V was measured. Devices initially had a relatively low conductance/area of 1 S/cm^2 . It was found that applying a voltage pulse of 3 to 4 V (corresponding to the voltage at peak current) created a high-conductance state. Devices in this state (measured at a voltage below 2.5 V) typically had a conductance/area of 10^3 S/cm^2 , representing an increase in conductance of 10^3 . Devices could be returned to a low-conductance state by applying a larger voltage pulse ($> 4 \text{ V}$). A typical programming sequence is shown in Figure 4. For simplicity, we will refer to the high-conductance state as the ON state, and programming into the ON state as a “write” operation; similarly, the low-conductance state is referred to as OFF, and programming into it an “erase” operation. The device begins in the OFF state, so that the 1-V “read” pulse returns a low current indistinguishable from noise. Next a 4-V pulse writes the device into the ON state that is read by the following read pulse. A 10-V erase pulse then returns the device state to the OFF state that is read by the final read pulse. Programmed states were stable for several hours, and devices have been operated tens of cycles without degrading.

The dependence of the conductance of the stored state on the programming voltage was investigated further by applying 1-ms voltage pulses of increasing amplitude to a device (initially in the OFF state), then measuring the resulting device conductance at 0.5 V. This dependence is shown in Fig. 5, along with a low-speed current-voltage scan for comparison. The programmed conductance does not change for voltage pulses below 2.5 V, indicating that voltages in this range can be used to read the device without destroying the programmed state. Above 2.5 V, the programmed conductance rapidly increases to a maximum near 3 V so that voltages between 3–4 V can be used to write the device into the ON state. Above 4 V, the programmed conductance decreases rapidly as the device is erased. Interestingly, the programmed conductance traces out a curve very similar to the NDR observed in current-voltage scans. This clearly suggests that

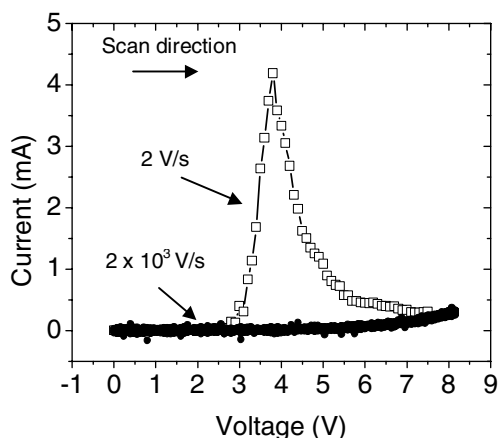


Figure 3. Current vs applied voltage for scan speeds of 2 V/s (hollow squares) and $2 \times 10^3 \text{ V/s}$ (solid squares).

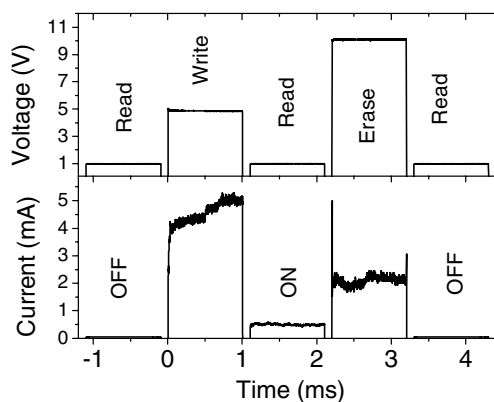


Figure 4. Typical programming sequence on a device with Au bottom and top electrodes. The device starts in the OFF state and is probed with 1-ms, 1-V read pulses that alternate with write (4-V) and erase (10-V) pulses to program the device into ON and OFF states.

the NDR is in fact a dynamic programming of the device into the high-conductance state near 4 V followed by a programming of the device into a low-conductance state at higher voltages. Preliminary measurements suggest that erasing occurs very quickly (<100 ns), while writing the device may take on the order of ms. In current-voltage measurements faster than this time scale (corresponding to measurement speeds $> 10^3$ V/s), the device will not have adequate time to be programmed into the high-conductance state. Therefore, we would not expect to observe NDR at these scan speeds, as was found experimentally (Fig. 3).

Replacing the top gold electrode with aluminum resulted in asymmetric device characteristics in low-frequency current-voltage scans (Fig. 6). When positive voltage was applied to the bottom gold electrode, an NDR characteristic similar to that observed in devices with two gold electrodes was obtained. However, NDR was not observed in scans with positive bias applied to the top aluminum electrode. The asymmetric NDR observed when one electrode is replaced with aluminum provides strong evidence that the mechanism for NDR and conductance programming is not inherent in the MUA layer and instead involves the metal electrodes. This conclusion is supported by the results of previous workers who have observed qualitatively similar characteristics in a variety of electroformed devices [7-9]. Most of the previous results have been obtained in much thicker, inorganic insulating films, although some similar work on organic films has recently been reported [10]. Most workers have concluded that the NDR and conductance switching involves metal ions or clusters that have been injected into the insulating layer. However, there is some disagreement over whether the actual mechanism is the movement of these metal ions/clusters, resulting in the formation and destruction of conducting paths in the insulator [8,11,12]; or charge-trapping leading to the creation of an electric field that lowers device conductivity [10,13].

In these films, the absence of NDR for positive bias on the aluminum electrode in devices with a top aluminum electrode suggests that a charge-trapping process is unlikely. If charge-trapping were responsible, the NDR would be observed regardless of bias (although the peak position may shift due to differing metal work functions). The observations instead support a

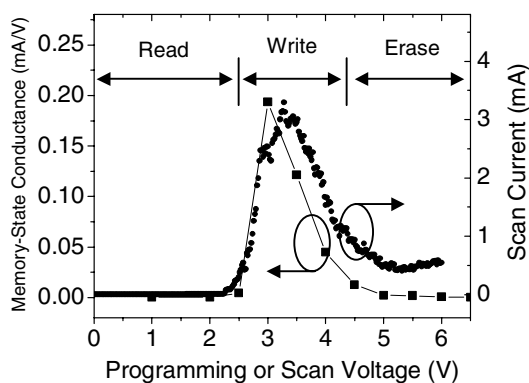


Figure 5. Memory-state conductance vs programming voltage (left axis); scan current vs applied voltage (right axis). The conductance of the memory state was measured at 0.5 V after application of a 1-ms programming pulse. In both cases, the (programming or scan) voltage was increased from 0.

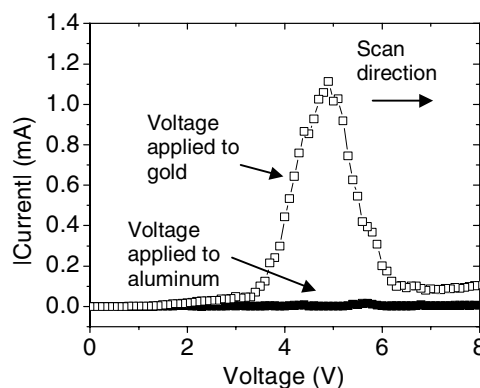


Figure 6. Current vs voltage applied to bottom gold electrode (hollow squares) or top aluminum electrode (solid squares) for a device with a bottom gold and top aluminum electrode.

model in which mobile gold (and not aluminum) forms conducting paths near 3 V; these paths can then be destroyed by joule heating at higher voltages to return to a low-conductance state. The details of this mechanism, including the conduction mechanism in the pathways formed by the gold and whether the movement of the gold is voltage- or thermally-driven, are currently under investigation.

CONCLUSIONS

We have observed symmetric NDR with very large peak current densities of up to 10^4 A/cm² in nanoscale films of the insulating molecule MUA contacted by gold electrodes. This NDR is due to a dynamic programming of the device into a high-conductance state near the NDR peak of 3-4 V followed by a programming into a low-conductance state at higher voltages. Short (1-ms) voltage pulses were used to program the device into high- and low-conductance states that were read non-destructively at lower voltages (< 2.5 V). These devices could therefore be operated as a reversible, nonvolatile memory with a dynamic range of 10^3 between ON and OFF states. Measurements on samples fabricated with one gold electrode and one aluminum electrode revealed asymmetric NDR and suggest that the mechanism for NDR and conductance switching in these devices is the movement of mobile gold atoms to create and destroy conducting pathways in the film. The large ON/OFF ratio and stability of the stored memory states make these devices attractive candidates for potential application as solid-state memory.

ACKNOWLEDGMENTS

This work was supported by ONR contract N00014-02-1-075 and the New Jersey Center for Organic Optoelectronics.

REFERENCES

1. C.-U. Pinnow and T. Mikoajick, *J. Electrochem. Soc.* **151**, K13 (2004).
2. J. A. Hutchby, G.I. Bourianoff, V. V. Zhirnov, and J. E. Brewer, *IEEE Circuits and Devices Magazine*, 28 (March 2002).
3. Y. Yang, L. P. Ma, and J. Wu, *MRS Bull.* **29**, 833 (2004).
4. S. D. Evans, A. Ulman, K. E. Goppert-Berarducci, and L. J. Gerenser, *J. Am. Chem. Soc.* **113**, 5866 (1991).
5. T. Graves-Abe, Z. Bao, and J.C. Sturm, *Nano Lett.* **4**, 2489 (2004).
6. L. Sanche, *Nuc. Inst. Meth. Phys. Res. B* **208**, 4 (2003).
7. J.G. Simmons and R. R. Verderber, *Proc. Roy. Soc. London Ser. A, Math. Phys. Sci.* **301**, 77 (1967).
8. G. Dearnaley, A. M. Stoneham, and D. V. Morgan, *Rep. Prog. Phys.* **33**, 1129 (1970).
9. A. K. Ray and C. A. Hogarth, *Int. J. Electronics* **57**, 1 (1984).
10. L. D. Bolzano, B. W. Kean, V. R. Deline, J. R. Salem, and J. C. Scott, *App. Phys. Lett.* **84**, 607 (2004).
11. S. Gravano, E. Amir, R. D. Gould, and M. Abu Samra, *Thin Solid Films* **433**, 321 (2003).
12. A. K. Ray and C. A. Hogarth, *Int. J. Electronics* **69**, 97 (1990).
13. R. E. Thurstans and D. P. Oxley, *J. Phys. D* **35**, 802 (2002).