Flexible Memristors Fabricated through Sol-Gel Hydrolysis

J.L. Tedesco, N. Gergel-Hackett, L. Stephey, M. Hernández-Mora, A.A. Herzing, L.J. Richter, C.A. Hacker, J.J. Kopanski, and C.A. Richter
National Institute of Science & Technology
100 Bureau Drive, Gaithersburg, MD 20899

Memristors have been identified as having a number of beyond-CMOS applications, such as smart interconnects [1] and neuromorphic circuit architectures [2]. Memristors have also been fabricated on flexible substrates [3], offering the possibility of integration with other flexible electronic devices, such as sensors, power supplies, identification tags, and visual displays. However, for a practical realization of these devices, a deeper understanding of the physical mechanisms behind the operation of flexible memristors must be obtained.

In this study, memristors were fabricated on flexible polyethylene terephthalate (PET) substrates with thermally evaporated aluminum contacts and an oxide film formed by using a sol-gel of titanium isopropoxide and ethanol. The final oxide thickness can be controlled by varying the relative amounts of ethanol and titanium isopropoxide within the sol-gel. Flexible memristors were fabricated in two sizes (2 mm × 2 mm and 100 µm × 100 µm) and with different oxide thicknesses (~8 nm, 17 nm, 33 nm, and 45 nm). Examples of the 2 × 2 mm^2 devices ("large area devices") and the 100 × 100 μm^2 devices ("small area devices") are shown in Fig. 1.

X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), and variable angle spectroscopic ellipsometry measurements suggest that while the oxide is essentially TiO_2, it is not present in an ordered crystalline form. The XPS and EELS measurements also indicate that a significant fraction of the film is amorphous organic material. Additionally, atomic force microscopy and optical profilometry measurements indicate that particularly for thicker films, the presence of the amorphous material gives the surfaces of the memristive devices a heterogeneous appearance. This appearance and the organic materials indicate that the structure of these solution-processed memristors is different from the apparent structure of the initial TiO_2-based memristors fabricated without the use of a sol-gel [4]. Such differences in appearance may presage differences in the physical mechanisms behind memristive behavior in flexible devices.

Elemental mapping via TEM suggest that the mottled appearance is not due to significant agglomerations of the constituent elements of the TiO_2 films, but can be attributed to differences in the actual thickness of the films. It is possible that such differences in thickness could lead to differences in the conduction across the oxide film, which may affect the switching mechanism within the device.

In order to investigate the switching mechanism in these memristors, the bias and sweep rate dependence of current-voltage (I-V) curves was studied. The bias necessary to switch the large area devices was constant, independent of TiO_2 thicknesses, whereas the switching bias for the small area devices were constant until the 45 nm TiO_2 thickness which switched at a larger applied bias. This behavior is inconsistent with an electric field induced switching mechanism. Sweep rate studies indicate some memristors remain in the "off-state" during short sweeps, but switch during slower sweeps of the same bias. This observed dependence of switching on the duration of the applied bias is suggestive that switching is induced by charge flow in the memristor.

Analysis of the I-V curves recorded from these devices indicates that following switching conduction is generally ohmic. However, sectioning a device that is in the "on-state" into two pieces reveals that conduction in one of the pieces remains ohmic, while conduction in the other piece becomes non-ohmic, suggesting that conduction in these flexible memristors is predominantly due to localized conduction pathways. Observance of a hot spot formed in thermal imaging measurements is further evidence that conduction occurs via localized current pathways.

Typical capacitance-frequency (C-f) and conductance-frequency (G-f) measurements of the devices are shown in Fig. 2. These measurements show a shift between the "on-state" and "off-state" of the device, indicating an additional loss mechanism in these films that is not present in ordinary TiO_2 films. This mechanism is attributed to dipoles in the organic constituents that are by-products of the sol-gel process.

References

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Figures

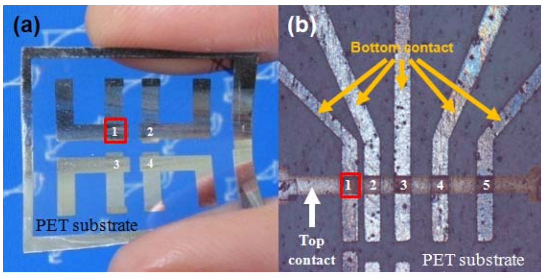

Fig. 1. (a) Photograph of four large area memristors fabricated on a PET substrate, which is being manually flexed. The area inside the box is the crossbar region of the memristor, measuring 2 × 2 mm^2. (b) Optical microscopy image of five small area memristors fabricated on a PET substrate. The area inside the box measures 100 × 100 μm^2 and the contacts are identified.

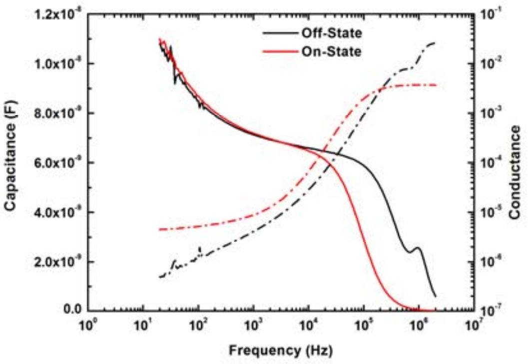

Fig. 2. C-f (solid) and G-f (dash-dot-dash) curves recorded from the same device (large area device, 17 nm thick TiO_2) while it was in the off-state and then in the on-state following switching. Conductance units are F/s.