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Drop-coated titanium dioxide memristors

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HIGHLIGHTS

- Full fabrication of a titanium dioxide sol–gel for use in drop-coated memristors is given.
- A thick film (37 microns thick) titanium dioxide layer gives good memristance.
- Aluminium foil tape electrodes work as well as sputter-coated aluminium electrodes.
- Drop-coated memristors do not require a forming step and start at low resistance.
- Switching gold electrodes for aluminium leads to device failure.

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ABSTRACT

The fabrication of memristors by drop-coating sol–gel $Ti(OH)_4$ solution onto either aluminium foil or sputter-coated aluminium on plastic is presented. The gel layer is thick, 37 μm, but both devices exhibit good memristance *I–V* profiles. The drop coated aluminium foil memristors compare favourably with the sputter-coated ones, demonstrating an expansion in the accessibility of memristor fabrication. A comparison between aluminium and gold for use as the sputter-coated electrodes shows that aluminium is the better choice as using gold leads to device failure. The devices do not require a forming step.

1. Introduction

Memristors have been credited with the possibility of revolutionising many areas of computational science such as memory [1] and neuromorphic computation [2,3]. Since the announcement of the first documented two-terminal memristor [1] (the first three-terminal memristor [4] having been made contemporary with Chua's theoretical prediction [5]) researchers have been eager to experiment with memristors, but they are difficult to synthesize and not yet commercially available. An important break-through in this area was the announcement of a solution processed memristor [6]. Although this memristor used the same 'memristive' material as Hewlett Packard (HP)'s nanoscale memristor, Titanium Dioxide (TiO_2), the electrode material was aluminium rather than platinum. The authors stated that the aluminium did not have an effect on the mechanism because switching was also seen with gold electrodes. However, another recently announced memristor device [7] with aluminium electrodes (with a graphene oxide substrate rather than TiO_2) has been shown to have different *I–V* characteristics if gold is used as an electrode. Similarly including Aluminium Oxide (Al_2O_3) in gold electrode and TiO_2 junctions was found to promote hysteresis [8]. Finally, it has been stated [1] and widely accepted that memristors should be nanoscale devices due to reasoning based on the device thickness term in equations presented in Ref. [1].

Resistive Random Access Memory (ReRAM) is a field closely associated with memristors. Its actual relation is controversial as it has been claimed that all resistive switching memories are memristors [9], this would implicitly include ReRAM devices, and similarly, it has been claimed that true memristors do not exist and reported memristors are actually ReRAM. We offer no opinion on this, but instead aim to discuss evidence from the ReRAM field that Al_2O_3 may be involved in TiO_2 memristors.

In the field of ReRAM there are two types of switching: Uni-Polar Switching (UPS) and Bi-Polar Switching (BPS) [10]. BPS closely resembles Chua's memristor plots, whereas UPS involves a much more definite jump in resistance values, usually an order of

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magnitude at least, although it still fits the definition for memristance. The memristive switching reported in Ref. [6] resembled UPS in that it has a large jump in resistance values. Both BPS and UPS have been reported in Pt/TiO_2/Pt electrodes [11] and resistive switching has been recorded in TiO_2 thin films grown by atomic layer deposition [12]. It might seem strange to attempt to compare different memristors/ReRAM devices made of similar materials fabricated in different ways, but Magnéli phases, a reduced-oxygen-content type of TiO_2, have been recorded in conduction filaments (widely believed to be the cause of switching in ReRAM, see for example [13]) in ReRAM devices and is implicated in memristor operation [14,15].

It is known that Al_2O_3 thin films undergo UPS [16] and that Al/anodized Al/Al devices can undergo resistive switching without needing a forming step. Al/Al_2O_3 based devices can even be fabricated on a flexible plastic substrate [16]. Al_2O_3 is implicated as being involved in TiO_2-based ReRAM switching as Election Energy-Loss Spectroscopy (EELS) of a Al/TiO_2/Al based resistive memory confirmed the presence of Al_2O_3 [17] and furthermore adding extra Al_2O_3 improved the operation of Al/TiO_2/Al memory [18].

In this paper, we present the creation of drop-coated Al/TiO_2/Al memristors, demonstrate that they undergo memristive BPS and compare results with aluminium and gold electrodes to elucidate whether Al_2O_3 might be involved in their operation. These devices can be synthesised with equipment available in a standard chemistry lab, simplifying the methodology still further and widening the field of researchers who can experiment with memristors.

2. Material and methods

Sol–gel preparation based on [6,19]. A three-necked flask was set-up to distill under flow of dried nitrogen, then glassware was pre-heated to 120 °C to remove water. 5 ml of titanium(IV)Isopropoxide 99.999%, 20 ml 2-methoxyethanol 99.9% and 2 ml ethanolamine 99+% were injected into the flask in that order, the mixture was then stirred for an hour at three temperatures, room temperature, 80 °C, 120 °C, before the resulting blood red solution in the reaction vessel was allowed to cool to room temperature. 10 ml of dry methanol was injected and the nitrogen flow turned off, after the vessel was filled with a positive nitrogen atmosphere, stoppered and left overnight to form a colourless $Ti(OH)_4$ (sol). A further 10 ml of methanol was injected to prevent atmospheric water from reacting with the sol. This was then further diluted 1:50 in dry methanol. For the aluminium substrate comparison aluminium electrodes were sputter-coated onto PET plastic.

The drop-coated memristors were fabricated using two different methods. For the simplest, two glass substrates were first covered in aluminium tape, with excess tape folded over and overhanging the edge of the glass to allow connections to the memristor. The 1:50 drop-coating solution was applied and left for half an hour in a clean fume hood (ambient air), until the white TiO_{2-x} (gel) layer was visible, before a second drop was added and allowed to dry. The uncoated aluminium tape was then cut away and removed from the glass, except for a narrow strip which acts as a connection to the aluminium-tape overhang. Both sides were given yet another drop of $Ti(OH)_4$(sol) and as soon as the methanol had evapourated the two substrates were assembled as a sandwich and taped together. The best results were achieved when the two substrates had the aluminium tape ‘wire’ at 90° to each other so the only place the two electrodes were closer to each other was where the sol had been deposited. The entire drop-coating process was completed within 1 h, the time $Ti(OH)_4$(sol) takes to convert to TiO_{2-x}(gel) [20]. To get a better aluminium surface, previously sputter-coated plastic was cut to shape, stuck to a glass substrate and then coated as above. In all devices the back of the glass substrate was covered in masking tape to prevent the measurement of glass surface effects at very low currents (10^{-11} A). Devices were left overnight to dry prior to measurement. Annealing the TiO_{2-x} (as suggested in Ref. [19]) was found to cause short-circuits. The general scheme of the device structure is shown in Fig. 1.

An approximate layer thickness calculated by preparing 14 double drops (as for assembling half the device) on aluminium tape covered glass surface that was previously weighed, allowed to dry in ambient air and weighed again. The actual layer thickness was verified by deconstructing a used device, slicing through it with a razor blade and using a Phillips XL-30 ESEM (Environmental Scanning Electron Microscope) to image it.

To investigate the TiO_2 layer, X-ray Photoelectron Spectroscopy, (XPS) and X-ray diffraction analysis (XRD) were carried out. XPS analysis was performed with a Thermo Fisher Scientific (East Grinstead, UK) Escascope equipped with a dual anode X-ray source (AlKα 1486.6 eV and MgKα 1253.6 eV). Samples were analysed under high vacuum ($<5 \times 10^{-8}$ mbar) with AlKα radiation at 250 W (12.5 kV; 20 mA). Following the acquisition of survey spectra over a wide binding energy range, the C 1s, O 1s, Al 2p, Si 2p and Ti 2p spectral regions were then scanned at a higher energy resolution such that valence state determinations could be made for each element. XPS data analysis was carried out using Pisces software (Dayta Systems, Bristol, UK) with binding energy values of the recorded lines referenced to the adventitious hydrocarbon C 1s peak at 284.8 eV. The XRD was performed with a Philips Xpert Pro diffractometer with a CuKα radiation source($\lambda = 1.5406$Å) was used for XRD analysis (generator voltage of 40 keV; tube emission current of 30 mA). XRD spectra were acquired between 2θ of 10–90°, with a step size of 0.02°and a 1 s dwell time. Phase identification was then performed using the ICDD (formerly JCPDS) spectral library and standard curve fitting software.

To elucidate the effect of aluminium, two types of memristors were made, those with two gold sputtered coated plastic electrodes and those with one gold-sputtered and one aluminium sputtered plastic electrode.

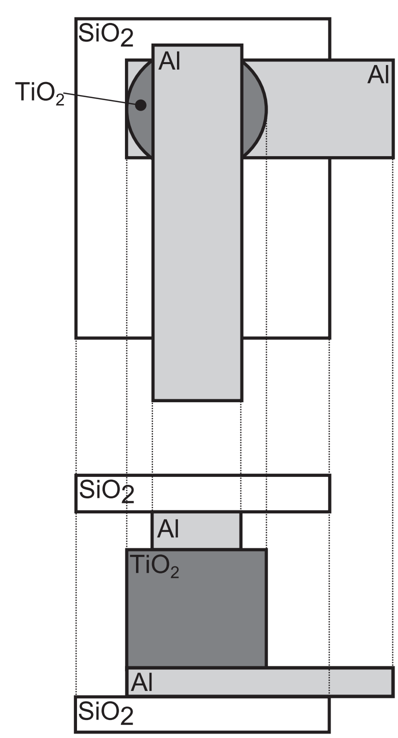

Fig. 1. Device schematic. Crossed aluminium electrodes mounted on glass drop-coated with *a*-TiO_2 sol–gel and sandwiched together.