Drop-coated Titanium Dioxide Memristors

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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, 14μm, 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.

Keywords: Memristor amorphous materials electrical properties electronic materials semiconductors sol-gel preparation

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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

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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].

Resistive Random Access Memory (ReRAM) is a field closely associated with memristors. Its actual relation is controversal 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 feild 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 magnitude at least, although it still fits the definition for memristance. The memristive switching reported in [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 Magneli phases, a reduced-oxygen-content type of TiO_2, has 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 film 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 flexable plastic substrate [17]. 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 [18] and furthermore adding extra Al_2O_3 improved the operation of $Al/TiO_2/Al$ memory [19].

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, 20]. A three-necked flask was set-up to distill under slow flowing dried nitrogen, then glassware was pre-heated to 120°C to remove water. 5ml of titanium(IV)Isopropoxide 99.999%, 20ml 2-methoxyethanol 99.9% and 2ml 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. 10ml of dry methanol was injected and the flowing nitrogen 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 10ml 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-coat solution was applied and left for half an hour, 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 that connected the drop to 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 accheived when the two substrates had the aluminium tape 'wire' at 90 degrees 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 hour, the time $Ti(OH)_4$(sol) takes to convert to TiO_{2-x}(gel) [21]. 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 [20]) was found to cause short-circuits.

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.

The memristors were measured on a Keithley 617 programmable electrometer which allowed the measurement of currents from pA-3.5mA. Measurements were performed with a dwell time of 2 seconds (unless otherwise mentioned), voltage step size of 0.05V and a measurement rate of 1s: this is the D.C. equivalent to an A.C. voltage frequency of 1mHz.

3. Results and Discussion

Figure 1 shows a typical I-V curve for one of the drop-coated memristors prepared on aluminium tape, those prepared on aluminium sputtered plastic were similar in form, but often had larger hysteresis, see figure 2. For both fabrication methods described above, these devices start off in a highly conducting, low resistance state and switch to a low conducting, high resistance state. Repeated trips round the I-V loop causes the resistance to drop as the resistance change is not fully reversed over the range of the I-V loop. In both cases the memristors go round the lobes clockwise.

For drop-coated memristors prepared on aluminium tape, 70% (n=10) of the memristors were good devices (defined as possessing both a pinched I-V curve and hysteresis) with the remaining being either short-circuited or unconnected. 75% (n=12) of drop coated memristors on aluminium sputtered-coated plastic were good. These data show that good results can be obtained with less than ideal aluminium surfaces and thicker titanium dioxide layers (the TiO_2 layer in these devices is circa 14μm thick, which is three orders of magnitude thicker than the nanoscale thin films in [1, 6]).

These devices require no forming step. We believe this is due to the fabrication method. Most of the ReRAM TiO_2 resistive memory devices were prepared by atomic layer deposition or a similarly controlled technique. TiO_2 memristors are believed to operate due to the movement of oxygen vacancies [1] and ReRAM is believed to be related to the formation of Magneli phase filaments, therefore there needs to be an oxygen deficiency somewhere in the material. The forming step creates this in vapour-deposited memristors/ReRAM. As drop-coated sol gel is far more amorphous, it already naturally contains areas with more oxygen vacancies, removing the need for

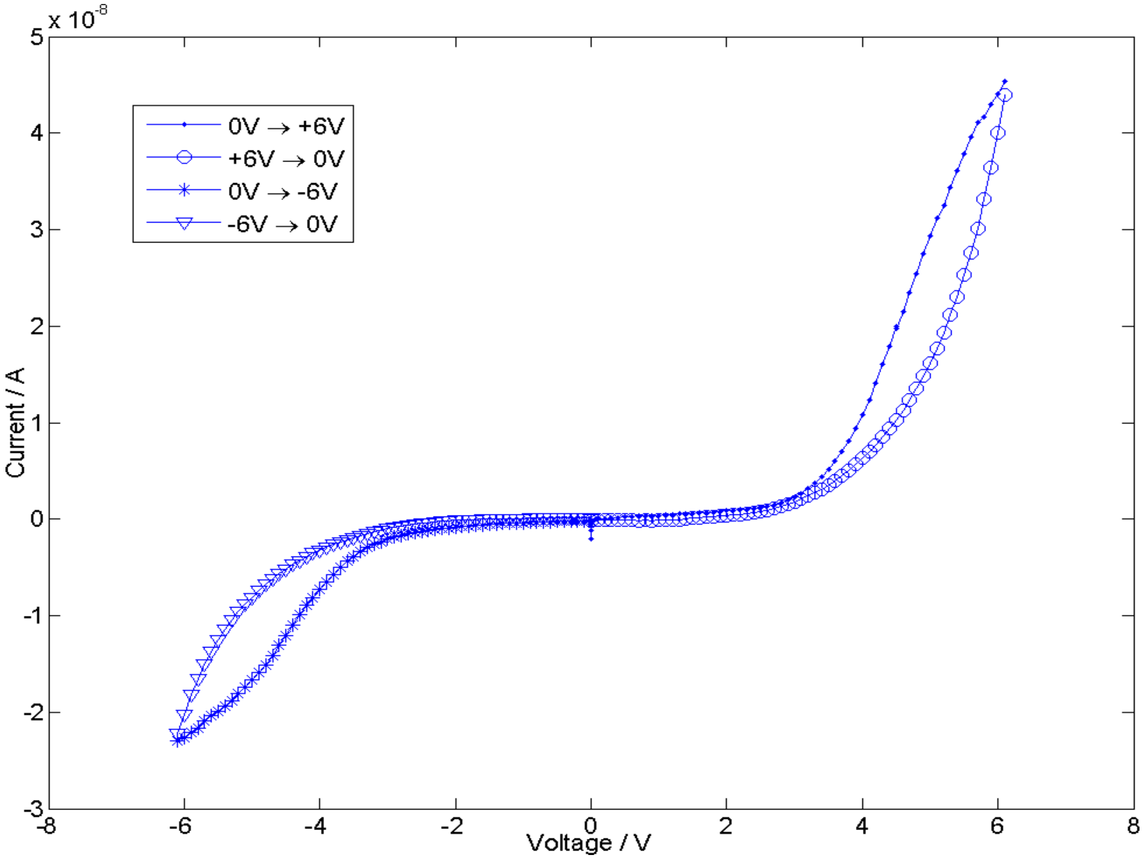

Figure 1: A macroscopic memristor made from aluminium tape. Note that the device increases resistance as it charges and has a larger positive than negative lobe. The I-V loop is pinched to zero current at zero voltage and goes around both sides of the curve in a clock-wise direction. This I-V shape is common in these memristors. This I-V curve was run with a 3 second dwell time.

a forming step. Note, there are many oxygen defects in these memristors because they start in the high conducting state and then switch to a lower one under the action of applied voltage.

To elucidate the role of aluminium in the mechanism, a batch of macroscopic gold sputter-coated electrode memristors were made. Of these, one was completely short-circuited, the others were not memristors: they had tiny currents (∼10 pA), straight-line profiles, no hysteresis and were comparable to the glass and aluminium electrodes test case (ie no semiconductor material).

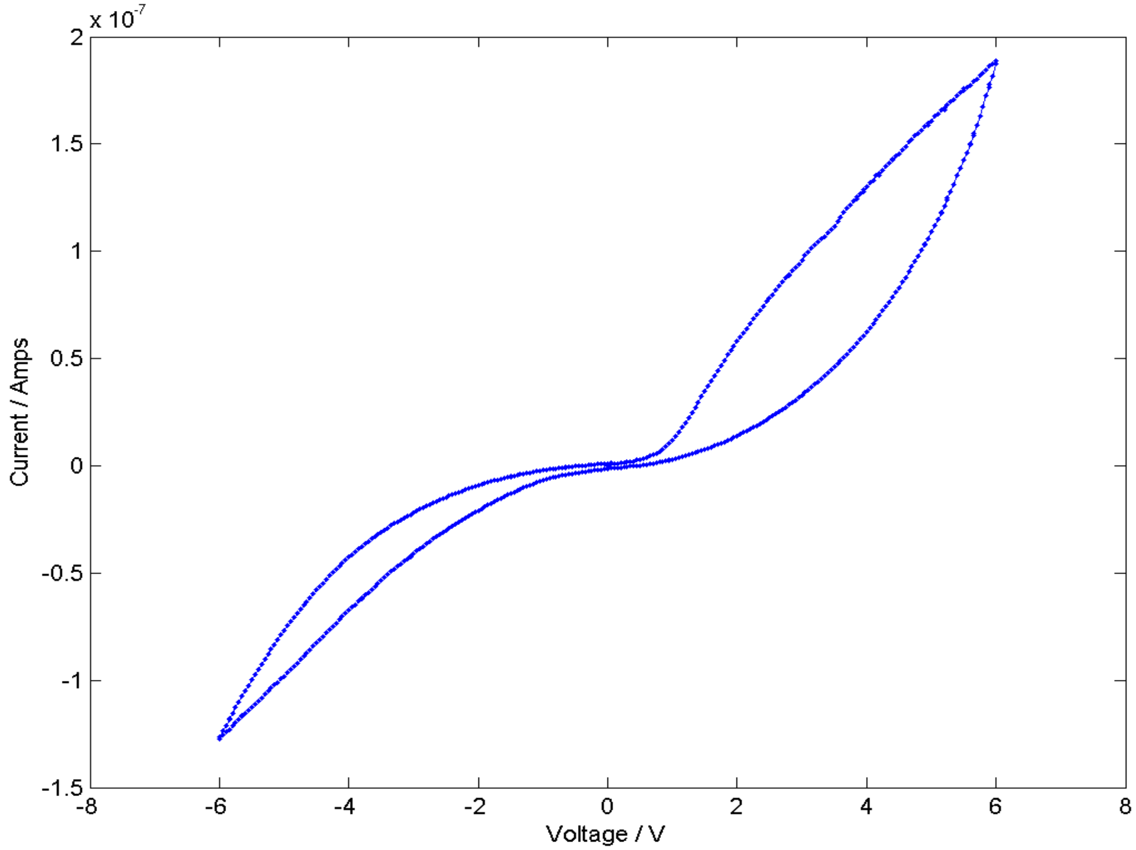

Figure 2: Typical I-V curve for a drop-coated memristor made with sputtered aluminium plastic electrodes. This device also shows the distinctive pinched hysteresis I-V curve.

The drop-coated memristors with one aluminium and one gold electrode show an extreme directionality in their I-V curves. Comparing the first runs of one such device, figure 3 demonstrates that the positive part of the I-V curve looks qualitatively similar to the that shown in figure 1 in that it has a large hysteresis loop. The negative side has much smaller hysteresis (even allowing for the non-rotational symmetry of these I-V curves). When we switch which electrode is the source and which is the drain, the other half of the I-V curve has memristor-like behaviour. Note, using the drop-coating technique, the thickness of the layer is not controlled, and thus the current, varies, therefore we can only compare the I-V curves between devices in a qualitative manner. These devices had a high failure rate: 58% (n=12) were short-circuited. Thus, the aluminium electrodes are an essential part in the

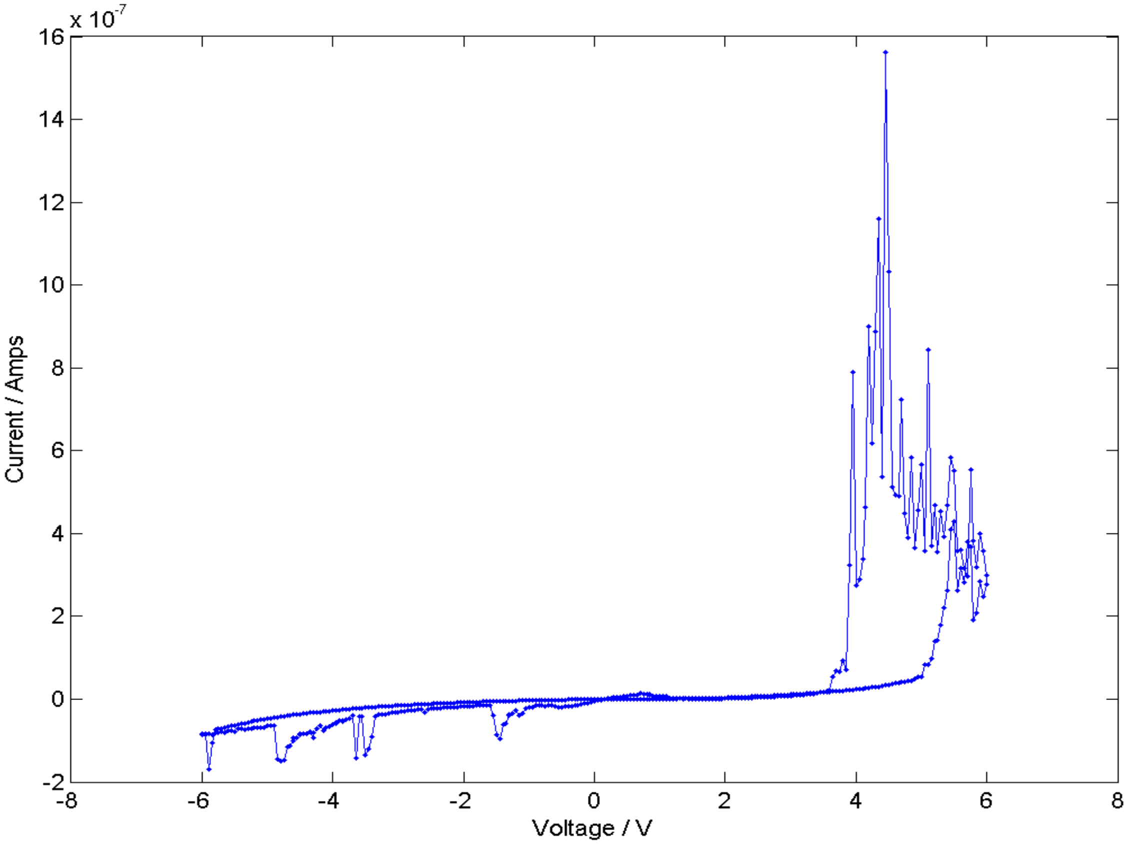

Figure 3: I-V curve for a memristor made with one aluminium and one gold sputtered electrode. The positive side of the curve shows the same type of behaviour when aluminium is the source. When these devices aer connected the other way round, the negative side only has appreciable hysteresis. Note the high failure rate of these devices may contribute to the noisiness of the curve.

operation of these drop-coated macroscopic memristors, without aluminium, there is no memristive switching.

4. Conclusions

A simpler method to make memristors for testing purposes has been demonstrated. It has been suggested that aluminium is an essential component for the operation of these sol-gel memristors. These memristors do not require a forming step. They have thicker titanium dioxide layers than those generally reported, showing that memristance does not require a nanoscale dimension within the device.

5. Acknowledgments

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6. Figure Legends

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