Aluminium Electrodes Effect the Operation of Titanium Oxide Sol-gel Memristors

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July 1, 2011

Abstract

By a comparison between memristors made with aluminium and gold electrodes, this letter demonstrates that aluminium electrodes are an essential component of the TiO_2 sol-gel flexible memristor . Both slow varying 'analogue' and sudden switching 'digital' memristor devices have been observed. Limiting the oxygen exposure of the bottom aluminium electrode favours the creation of digital memristors over analogue ones. A straight-forward fabrication of drop-coated memristors based on sol-gel chemistry is also presented and these show similar behaviour and dependence on electrode material, making them useful as test memristors for experimentation.

1 Introduction

Memristors have been credited with the possibility of revolutionising many areas of computational science such as flash memory and neuromorphic computation [1] [2]. Since the announcement of the first documented two-terminal

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[‡] E. Gale would like to acknowledge the support of EPSRC grant EP/HO14381/1

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memristor [2] (the first three-terminal memristor [3] having been made contemporary with Chua's theoretical prediction [4]) researchers have been eager to experiment with memristors, but they difficult to synthesize and are not commercially available. An important break-through in this area was the announcement of a solution processed memristor [5]. Although this memristor used the same 'memristive' material as 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 [6] 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. Including Al_2O_3 in gold electrode and TiO_2 junctions was found to promote hysteresis [7]. In this paper, we will suggest that the I-V characteristics of the flexible memristor is related to the effects of aluminium oxide.

In order to achieve this, we followed the preparation in [5], but also made macroscopic drop-coated memristors for comparison. These thick layer 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. Both sets of devices show a richer range of behaviours than previously reported.

2 Methodology

Sol-gel preparation based on [5, 8]. 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 $\mathrm{Ti(OH)_4}$ (sol). A further 10ml of methanol was injected to prevent atmospheric water from reacting with the sol. This was then further diluted in dry methanol, 1:10 for the spin-coat solution and 1:50 for the drop-coat solution.

For the nanoscale memristors, two sheets of aluminium electrodes were sputter-coated onto PET plastic. To compare the effect of two different amounts of Aluminium oxide, one was immediately put under vacuum, one was left in the clean room air overnight. Both were then spun-coated with 3ml of 1 in 10 $\mathrm{Ti(OH)_4}$ in methanol solution to give a gel layer 44nm thick. The solution was then left for two hours in the clean room environment to hydrolyze, before the second set of electrodes were sputtered on top. The vacuum-exposed electrode was exposed to air for less than 2 minutes before being spin-coated; it is expected that the air-exposed electrode would have a thicker layer of aluminium oxide.

The drop-coated memristors were fabricated by a two different methods. For the simplest, a glass substrate was first covered in aluminium tape, then 1:50 drop-coat solution was drop-coated on and left for about half an hour, until the white $\mathrm{TiO_{2-x}}$ gel layer was visible, then a second drop was added and allowed to dry. The uncoated aluminium tape was cut away, except for a narrow strip that connected to the aluminium-tape electrodes, and then both sides were given yet another drop of $\mathrm{Ti(OH)_4}$(sol) and as soon as the methanol had evapourated the device was assembled (two drop-coated electrodes at 90°and on top of one another) and taped in place. The entire drop-coating process was all done within 1 hour, the time $\mathrm{Ti(OH)_4}$(sol) takes to convert to $\mathrm{TiO_{2-x}}$(gel) [9]. To get a better aluminium surface, previously sputter-coated plastic was cut to shape, stuck to a glass substrate and then coated, the solution was more wetting on this surface and thus 4-5 drops were used on each side. 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. Devices were left overnight to dry prior to measurement.

To elucidate the effect of aluminium on the nanoscale memristors, gold sputter-coated memristors were prepared as above. For the macroscopic drop-coated method, 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-3.5nA. Some memristors went above this range, and were thus considered high current. Most 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

3.1 Drop-coated Memristor

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. For both macroscopic 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 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.

3.2 The Effect of Gold

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).

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 2(b) and an early prototype of the two aluminium electrode memristor, figure 2(a), we can see that the positive part of the I-V curve looks qualitatively the same. 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, that with the drop-coating technique, the thickness of the layer, and thus the current, varies wildly, 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.

8% (n=12) nanoscale memristors with aluminium sputtered electrodes were short-circuited, 100% (n=25) nanoscale memristors with gold sputtered electrodes were short-circuited, with an average resistance of 13Ω and no memristor-like I-V curve.

The aluminium electrodes are an essential part in the operation of both the spun-coated nanoscale and drop-coated macroscopic memristors, without them, there is no memristive switching.

3.3 Behaviour of the Nanoscale Memristors

The nanoscale memristors were found to have three types of behaviours. The simplest was acting like linear ohmic resistors. The second type was curved memristance profiles which were qualitatively similar to those seen in the drop-

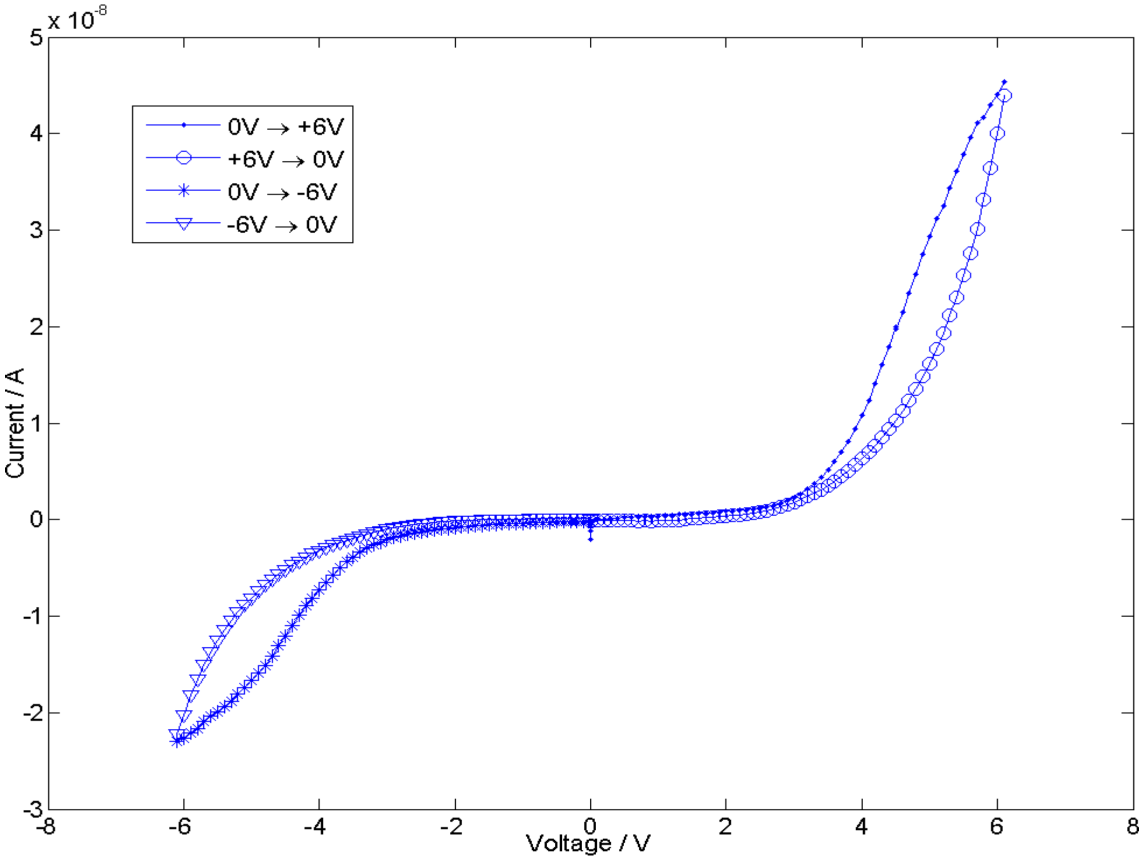

Figure 1: A macroscopic memristor made from aluminium tape. Note that the device increases resistance as it charges and has a larger positive than negative lobe. The I-V loop is pinched to zero current at zero voltage and goes around both sides of the curve in a clock-wise direction. This sort of shape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

Table 1: How the effect of aluminium oxide changes the behaviour of virgin memristor devices. % rounded up to the nearest whole number. Twelve devices were measured in each data set.

Bottom Al electrode exposed to	I-V profile shape		
	Analogue	Digital	Linear
Air	25%	42%	33%
Vacuum	17%	67%	17%

coated memristors. These had slow varying I-V curves which would be useful for analogue computation. The third, and most common type, were the sudden switch I-V curves very similar to those previously reported [5]. This type of behaviour is useful for digital switches.

Table 1 demonstrates that extra aluminium oxide promotes a greater variety of device types, whereas keeping the aluminium layer as pristine as possible favours memristors that switch more suddenly. Conducting filament switching mechanisms have been observed [10] for TiO_2: a sudden connection of a conducting filament could cause sudden switching. This might suggest that the analogue devices have a different switching mechanism, but some caution needs to be exercised: it could simply be that the natural frequency of the devices is affected and thus which type of behaviour is observed in this study. How the aluminium oxide is effecting the device mechanism is also an open question. However, Al_2O_3 inserted in titanium dioxide junctions was shown to produce analogue style I-V curves [7], so perhaps a layer of aluminium oxide is promoting analogue switching relative to the filament switching.

There is a similarity between the analogue shaped I-V curves in both the thick and thin film memristors, suggesting a similar mechanism, despite the variation in TiO_2 layer. That the results from the comparisons with gold electrodes are similar in the two types of devices also supports this suggestion. If correct, the flexible memristors have a different mechanism to that reported by Stan Williams' group, even though their device is also made with TiO_2. A recent review [11] has highlighted the multitude of titanium dioxide stochiometries that could be involved in the operation of these memristors, so it is possible that two differently manufactured TiO_2 memristors could have different mechanisms.

4 Conclusion

A simpler method to make memristors for testing purposes has been demonstrated. From two sets of comparisons based on drop-coated memristors and nanoscale thick TiO_2, it has been ascertained that the aluminium is an essential component for the operation of sol-gel memristors. Two useful types of switching, slow 'analogue' and fast 'digital', have been observed in both types of devices, and it has been suggested that the relative proportions of these two switching mechanisms could be due to the thickness of the aluminium oxide layer.

Acknowledgment

The authors would like to thank Richard Ewen for helpful advice.

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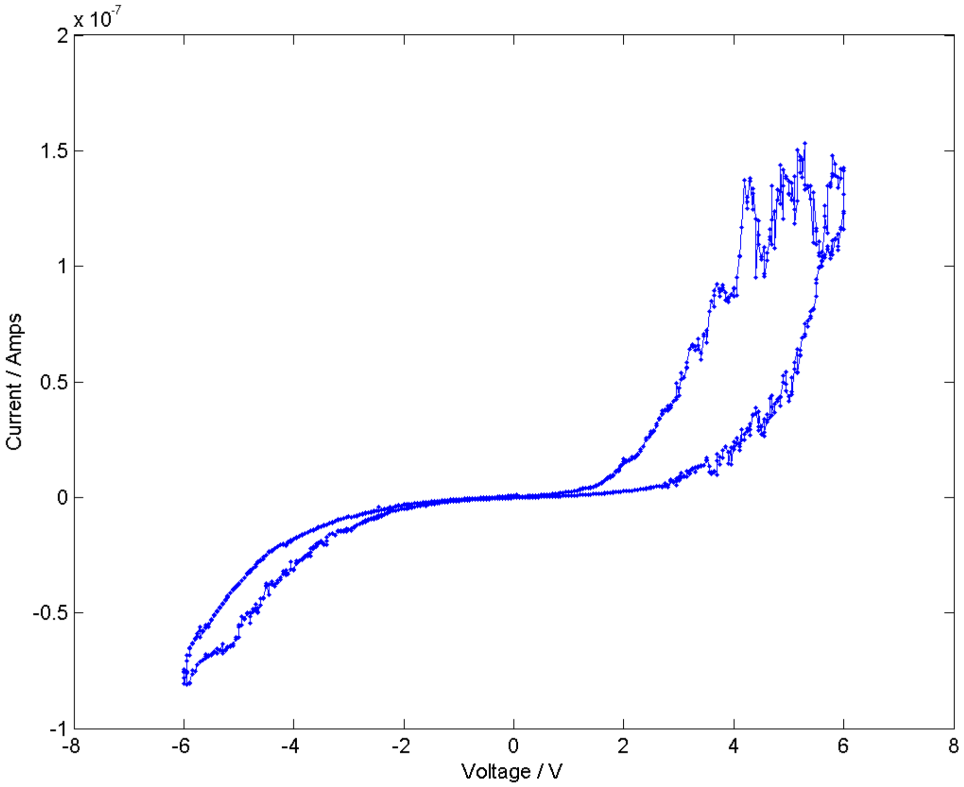
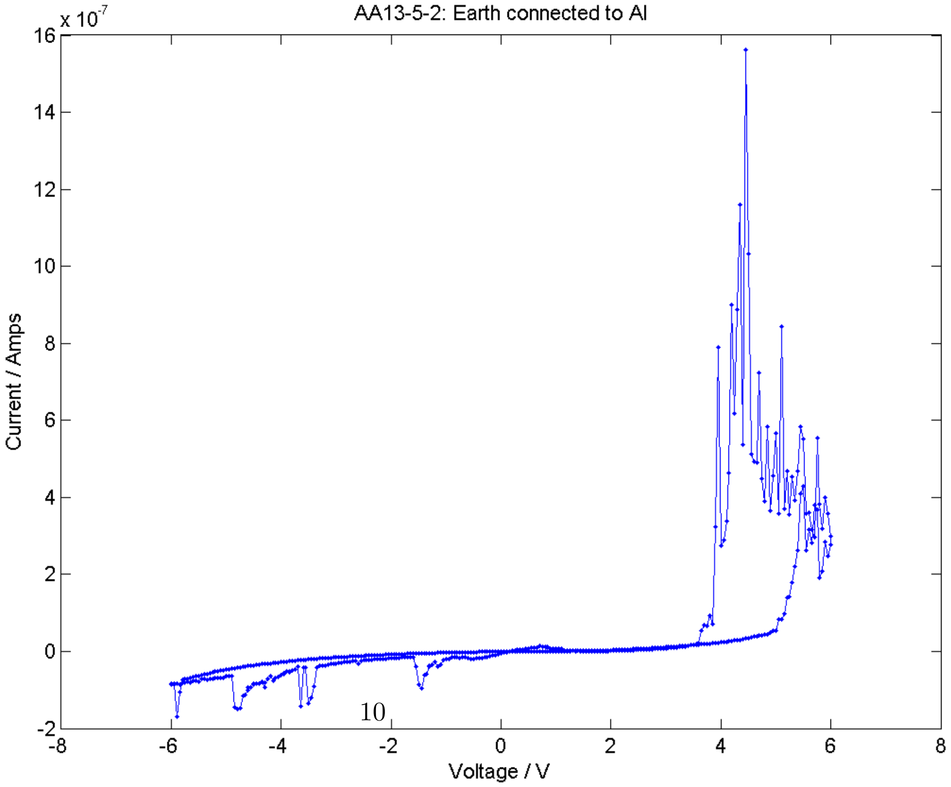


(a) Case I



(b) Case II

Figure 2: 2(a) is an 2 aluminium sputtered electrode macroscopic memristor, 2(b) is a memristor made with one aluminium and one gold sputtered electrode.