Solution-processed, low voltage tantalum-based memristive switches

DOI:

[10.1016/j.matlet.2020.127676](https://doi.org/10.1016/j.matlet.2020.127676)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Sophocleous, M., Mohammadian, N., Majewski, L. A., & Georgiou, J. (2020). Solution-processed, low voltage tantalum-based memristive switches. *Materials Letters*, 269, 127676. <https://doi.org/10.1016/j.matlet.2020.127676>

Published in:

Materials Letters

Citing this paper

Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights

Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy

If you believe that this document breaches copyright please refer to the University of Manchester's Takedown Procedures [<http://man.ac.uk/04Y6Bo>] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.

Solution-processed, low voltage tantalum-based memristive switches

Marios Sophocleous^{1*}, Navid Mohammadian², Leszek A. Majewski² and Julius Georgiou¹

¹Holistic Electronics Research Laboratory, Department of Electrical and Computer Engineering, EMPHASIS Research Centre, University of Cyprus, Nicosia, Cyprus

²Department of Electrical & Electronic Engineering, The University of Manchester, Manchester, M13 9PL, United Kingdom

Abstract— In this letter, preliminary results showing the memristive behavior of tantalum/tantalum oxide/platinum devices on glass substrates are reported. The ultra-thin ($d < 10$ nm) tantalum oxide films were obtained using solution-based anodic oxidation (anodization) of Ta in citric acid. The devices were tested using standard ReRAM characterization tests from ± 0.5 V to ± 5 V and showed a promising memristive behavior. The memristive switches show an almost 80-times change in resistance between the ON and OFF states.

Index Terms— Memristors, Memristive Switches, Anodization, Tantalum, Tantalum-Oxide

1. INTRODUCTION

Metal oxide dielectrics have drawn a lot of attention in recent years due to their use in the fabrication of high performance thin film capacitors (TFCs) [1], low voltage thin film transistors (TFTs) [2], and memristor devices [3]. However, the next generation of thin film electronic devices and systems will require reduced power consumption and the development of dielectric materials that can be inexpensively deposited from solution on large areas as a thin film is urgently needed [4]. Recently, anodic oxidation (so-called anodization) has attracted a lot of attention because it is a low cost, solution-based deposition process that can be used to fabricate high quality, ultra-thin metal oxide films [5]. Anodization is a self-limiting and self-healing process that gives pinhole-free, homogenous oxide layers grown in an ambient atmosphere at room temperature using low cost set-ups and environmentally friendly chemicals. Tantalum/tantalum oxide (Ta/TaO_x) memristive switches have been reported to show superior performance compared to other structures in terms of volatility [6], low voltage [7] and switching times [8]. They have been investigated by researchers to be used in ReRAM applications and more recently in neuromorphic computing since they can be used as neural synapses [9,10]. However, they are usually fabricated using expensive and sophisticated techniques such as multi-step RF sputtering and aggressive chemicals.

In this letter, the memristive behavior of tantalum/tantalum oxide/platinum ($\text{Ta}/\text{TaO}_x/\text{Pt}$) switches is reported. The TaO_x films were fabricated using low-cost anodic oxidation in a weak, naturally occurring acid. We show that the performance of the reported devices is comparable or indeed better than most of the previously reported $\text{Ta}/\text{TaO}_x/\text{Pt}$ memristors.

2. DEVICE PHYSICS

The complete picture of the charge transport in tantalum oxide memristors is still evolving [11] however, some common understanding revolves around three main points. Firstly, the charge transport in the ON state is dominated by an electroformed channel or filament within the tantalum oxide layer. The larger the filament radius and the smaller the oxide thickness the lower the ON resistance and the lower the forming voltage [12]. Secondly, the ratio of Ta:O within and around the active channel shows a significant change from the original ratio. Tantalum gets reduced to a lower oxidation state at the center and its oxidation state increases moving away from the center of the filament [12]. Lastly, the crystal structure of the material within and around the active channel plays an important role. The initially amorphous structure is changed to a nanocrystalline phase, which indicates local heating [13]. Hence, fabrication parameters can play a major role in the performance of the devices since the material stoichiometry and device behavior can greatly be affected by the fabrication process and environmental conditions.

3. MEMRISTOR FABRICATION

The devices were fabricated on 2×1.5 mm², quartz-coated glass substrates (Ossila, UK). Firstly, the substrates were rinsed with deionized (DI) water, dried with pure Nitrogen (N_2) and sonicated for 30 minutes in acetone, methanol and isopropyl alcohol (IPA) where they were finally dried with pure N_2 . Any residual organic contaminants were removed using an UV Ozone cleaner for 30 minutes. Ta strips with 100 nm thickness were initially deposited as the bottom

* Corresponding author, Email: sophocleous.marios@ucy.ac.cy

electrode using a shadow mask onto the cleaned substrates by radio frequency (RF) magnetron sputtering with a 2-inch Ta target (Kurt J. Lesker, 99.9% pure) at a power of 70 W in a pure Argon (Ar) atmosphere with a total pressure of 0.5 Pa at room temperature. Afterwards, the patterned Ta films were anodically oxidized in ambient conditions using 1 mM aqueous solution of citric acid ($\geq 99.5\%$, Sigma-Aldrich) (Figure 1). A Keithley 2400 Source-Measure-Unit was used to carry out the anodization process.

Figure 1: (left) Schematic of the setup for anodizing of Ta, (right) Anodization current (I_A) and voltage (V_A) vs. anodization time.

Details on the anodization procedure can be found elsewhere [14] however, the approximate thickness of tantalum oxide films was estimated to be ~ 7 nm. Finally, platinum (Pt) film of 50 nm thickness was deposited as the top electrode through a shadow mask using a 2-inch Pt target (Kurt J. Lesker, 99.9% pure) at a power of 50 W in a pure Ar atmosphere with a total pressure of 0.5 Pa at room temperature. The size of the fabricated memristive switches was $300 \times 400 \mu\text{m}^2$ (Figure 2).

Figure 2: (left) A cross section of the Ta/TaO_x/Pt devices, (right) 3D schematic of the fabricated device arrays.

4. EXPERIMENTAL SETUP

The devices were tested using Keithley 4200 Semiconductor Analyzer with two ultra-fast pulsing modules 4225RPM and the 4225-PMU card. The devices were tested using Signatone S-1160 probe station with the S-4210-MMPC-L multi-measurement prober cable kit. Short voltage pulses were sent and the current were recorded simultaneously. The Pt electrode was connected to the ground and pulses were sent to the Ta electrode. In all tests, PMU card was used to send the pulses and the current was measured at the ground terminal. Two consecutive pulses were sent, a negative and positive pulse with an intermediate delay of $20 \mu\text{s}$, whilst the rise/fall time and width time of each pulse was set to $1 \mu\text{s}$. A compliance current was set to $100 \mu\text{A}$ and the amplitude of the pulse was successively increased from ± 0.5 V to ± 5 V.

5. RESULTS & DISCUSSION

The devices began to behave like memristors at ± 4.5 V and a symmetrical I-V curve was obtained with 4.5 V and -5 V (Figure 3). These measurements were taken from $300 \times 400 \mu\text{m}^2$ devices however, typical memory element sizes are in the range of $1 \times 1 \mu\text{m}^2$ squares hence, the measurements were normalised to $\text{nA}/\mu\text{m}^2$. During stage 1, the devices were switched OFF completely and the resistance was calculated by fitting a line to the linear section of the graph. The linear fit (green line) has an R^2 of 0.97 and a resistance of $\sim 788 \text{ k}\Omega$ during the OFF state. The ON state resistance was calculated to be $10 \text{ k}\Omega$ in a similar fashion. However, only the top right quadrant was considered to ensure that only the current state would be measured. The linear fit (blue line) for the ON state has an R^2 of 0.86 due to some minor capacitance effects close to zero voltage.

Figure 3: A representative I-V characteristic showing the memristive behavior of the fabricated Ta/TaOx/Pt devices.

These values show an almost 80-times change in resistance between the ON and OFF states with maximum current of $0.83 \text{ nA}/\mu\text{m}^2$ showing promising potential for high-density applications. The performance of the reported devices is comparable or indeed better than the most of the previously reported Ta memristors in terms of $R_{\text{OFF}}/R_{\text{ON}}$ ratio using a $100 \mu\text{A}$ compliance current (Table 1).

Table 1: Performance comparison of the fabricated Ta/TaOx/Pt memristors with previously published works.

No	R_{ON}	R_{OFF}	$R_{\text{OFF}}/R_{\text{ON}}$	Compliance	Reference
1	$25 \text{ k}\Omega$	$\sim 100 \text{ k}\Omega$	~ 4	$100 \mu\text{A}$	[15]
2	-	-	>10	5 mA	[16]
3	$\sim 300 \Omega$	$80 \text{ k}\Omega$	~ 267	$300 \mu\text{A}$	[17]
4	$20 \text{ k}\Omega$	$800 \text{ k}\Omega$	40	$10 \mu\text{A}$	[18]
5	350Ω	$\sim 1.4 \text{ k}\Omega$	4	-	[11]
6	$\sim 10 \text{ k}\Omega$	$\sim 800 \text{ k}\Omega$	80	$100 \mu\text{A}$	This work

6. CONCLUSION

A low cost, solution-based fabrication procedure of Ta/TaOx/Pt memristive devices that can be formed and operated at voltages $\leq \pm 5 \text{ V}$ is presented. The devices feature resistances of $788 \text{ k}\Omega$ and $10 \text{ k}\Omega$ during the OFF and ON states, respectively. It has been demonstrated that the devices have an almost 80-times change in resistance with $0.83 \text{ nA}/\mu\text{m}^2$, without the need of expensive fabrication procedures. Although further work is required for complete device characterization including measurements of uniformity, retention, and endurance, this work illustrates the high potential of anodization as a low cost, environmentally friendly manufacturing technique for high performance memristors with the possibility of being compatible with CMOS and other VLSI fabrication technologies.

ACKNOWLEDGMENT

The authors would like to thank the University of Cyprus for the internal funds (Post-Doctoral Researchers - Advanced Level) and the MemoCiS COST Action IC1401 for the support and networking. N. M. and L.A.M. would like to thank UGC-UKIERI for financial support (Grant no. 2017/18-015).

REFERENCES

- [1] K.M. Yu, H.M. Ji, M.C. Nguyen, A.H.T. Nguyen, S.J. Choi, J.G. Cheon, J.H. Kim, S.W. Kim, S.Y. Cho, R. Choi, Low-Temperature Fabrication of High Quality Gate Insulator in Metal-Oxide-Semiconductor Capacitor Using Laser Annealing, *IEEE Electron Device Lett.* 40 (2019) 167–170. doi:10.1109/LED.2018.2889346.
- [2] E. Fortunato, P. Barquinha, R. Martins, Oxide semiconductor thin-film transistors: A review of recent advances, *Adv. Mater.* 24 (2012) 2945–2986. doi:10.1002/adma.201103228.
- [3] M.V. Diamanti, R. Pisoni, A. Cologni, A. Brenna, F. Corinto, M.P. Pedferri, Anodic oxidation as a means to produce memristive films, *J. Appl. Biomater. Funct. Mater.* 14 (2016) e290–e295. doi:10.5301/jabfm.5000290.
- [4] A.A. Ojo, I.M. Dharmadasa, Electroplating of semiconductor materials for applications in large area electronics: A review, *Coatings.* 8 (2018). doi:10.3390/coatings8080262.
- [5] S. Stathopoulos, A. Khiat, M. Trapatseli, S. Cortese, A. Serb, I. Valov, T. Prodromakis, Multibit memory operation of metal-oxide Bi-layer memristors, *Sci. Rep.* 7 (2017) 1–7. doi:10.1038/s41598-017-17785-1.
- [6] S. Choi, S. Jang, J.H. Moon, J.C. Kim, H.Y. Jeong, P. Jang, K.J. Lee, G. Wang, A self-rectifying TaO_y/nanoporous TaO_x memristor synaptic array for learning and energy-efficient neuromorphic systems, *NPG Asia Mater.* 10 (2018) 1097–1106. doi:10.1038/s41427-018-0101-y.
- [7] E. Kyriakides, S. Carrara, G. De Micheli, J. Georgiou, Low-cost, CMOS compatible, Ta 2O₅-based hemi-memristor for neuromorphic circuits, *Electron. Lett.* 48 (2012) 1451–1452. doi:10.1049/el.2012.3311.
- [8] A.C. Torrezan, J.P. Strachan, G. Medeiros-Ribeiro, R.S. Williams, Sub-nanosecond switching of a tantalum oxide memristor, *Nanotechnology.* 22 (2011). doi:10.1088/0957-4484/22/48/485203.
- [9] A. Serb, J. Bill, A. Khiat, R. Berdan, R. Legenstein, T. Prodromakis, Unsupervised learning in probabilistic neural networks with multi-state metal-oxide memristive synapses, *Nat. Commun.* 7 (2016) 1–9. doi:10.1038/ncomms12611.
- [10] Z. Wang, M. Yin, T. Zhang, Y. Cai, Y. Wang, Y. Yang, R. Huang, Engineering incremental resistive switching in TaO_x based memristors for brain-inspired computing, *Nanoscale.* 8 (2016) 14015–14022. doi:10.1039/C6NR00476H.
- [11] J.P. Strachan, A.C. Torrezan, F. Miao, M.D. Pickett, J. Joshua Yang, W. Yi, G. Medeiros-Ribeiro, R. Stanley Williams, State dynamics and modeling of tantalum oxide memristors, *IEEE Trans. Electron Devices.* 60 (2013) 2194–2202. doi:10.1109/TED.2013.2264476.
- [12] J.P. Strachan, G. Medeiros-Ribeiro, J.J. Yang, M.X. Zhang, F. Miao, I. Goldfarb, M. Holt, V. Rose, R.S. Williams, Spectromicroscopy of tantalum oxide memristors, *Appl. Phys. Lett.* 98 (2011). doi:10.1063/1.3599589.
- [13] F. Miao, J.P. Strachan, J.J. Yang, M.X. Zhang, I. Goldfarb, A.C. Torrezan, P. Eschbach, R.D. Kelley, G. Medeiros-Ribeiro, R.S. Williams, Anatomy of a nanoscale conduction channel reveals the mechanism of a high-performance memristor, *Adv. Mater.* 23 (2011) 5633–5640. doi:10.1002/adma.201103379.
- [14] N. Mohammadian, S. Faraji, S. Sagar, B.C. Das, M.L. Turner, L.A. Majewski, One-Volt , Solution-Processed Organic Transistors with Self-Assembled Monolayer-Ta₂O₅ Gate Dielectrics, *Materials (Basel).* 12 (2019).
- [15] P. Mickel R., C. James D., A. Lohn, M. Marinella, A. Hsia H., Methods for resistive switching of memristors, US9336870B1, 2016. doi:10.1109/IIRW.2012.6468.
- [16] P.R. Mickel, A.J. Lohn, B. Joon Choi, J. Joshua Yang, M.X. Zhang, M.J. Marinella, C.D. James, R. Stanley Williams, A physical model of switching dynamics in tantalum oxide memristive devices, *Appl. Phys. Lett.* 102 (2013). doi:10.1063/1.4809530.
- [17] K. Skaja, M. Andrä, V. Rana, R. Waser, R. Dittmann, C. Baeumer, Reduction of the forming voltage through tailored oxygen non-stoichiometry in tantalum oxide ReRAM devices, *Sci. Rep.* 8 (2018) 1–7. doi:10.1038/s41598-018-28992-9.
- [18] T. Ohno, S. Samukawa, Resistive switching in a few nanometers thick tantalum oxide film formed by a metal oxidation, *Appl. Phys. Lett.* 106 (2015). doi:10.1063/1.4919724.