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Total number of authors: 11

Published in:
A I P Advances

Link to article, DOI:
10.1063/5.0004722

Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):

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Cite as: AIP Advances 10, 065112 (2020); https://doi.org/10.1063/5.0004722
Submitted: 14 February 2020 . Accepted: 11 May 2020 . Published Online: 05 June 2020

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AIP Advances 10, 065112 (2020); doi: 10.1063/5.0004722

ABSTRACT

A key step in engineering resistive switching is the ability to control the device switching behavior. Here, we investigate the possibility to tune the resistive switching of tantalum oxide (TaOx)-based memristors from a non-switchable state to a switchable state by applying post-fabrication annealing of the devices. The switching of the devices was found to be related to: (1) the oxidation state changes in the TaOx thin film after annealing and (2) the local variations in oxygen stoichiometry in the vicinity of the interface between the TiN electrode and the TaOx active resistive layer. We further discuss the possible mechanism behind the resistive switching after annealing. This experimental approach provides a simple but powerful pathway to trigger the resistive switching in devices that do not show any resistive switching initially.

I. INTRODUCTION

Tantalum oxide (TaOx) is widely used as a resistive switching material in memristors as it exhibits excellent features such as superior endurance of more than 10^{12} cycles and ultra-fast switching speed of sub-nanoseconds. Tantalum oxide is a complex system that includes more than 20 non-equilibrium phases and two equilibrium Ta2O5 (tantalum pentoxide) phases. Being able to control these phases is an essential step in achieving highly controllable resistive switching behaviors in tantalum oxide memristors.

Two simple but effective methods that enable to tune and control the tantalum oxide (TaOx)-based memristor behaviors are: (1) manipulating the TaOx thin film growth conditions or/and (2) annealing the TaOx thin film after deposition. We have shown in our previous work that we can fine tune and control the resistivity of the TaOx thin film during the growth by pulsed laser deposition (PLD). By varying the oxygen pressure during deposition from 10^{-6} to 2 \times 10^{-2} mbar, the resistivity of the deposited tantalum oxide can be altered by more than six orders of magnitude as a result of a controlled oxygen stoichiometry. This, in turn, led to different resistive switching behaviors of the memristors. Memristors with TaOx deposited at low oxygen pressure below and equal to 2 \times 10^{-3} mbar showed no resistive switching, whereas TaOx deposited at oxygen pressures above 2 \times 10^{-3} mbar showed a resistive switching character.

Besides varying the oxygen pressure during thin film deposition, the annealing temperature is another critical factor influencing TaOx phases. For example, a Ta2O5 pellet after being sintered at 1400–1600°C for 24 h shows a monoclinic to orthorhombic phase transition by Raman scattering at about 327°C. Ta2O5 in an amorphous state (a-Ta2O5) transfer into low-temperature (LT) crystalline state (orthorhombic β-phase) at approximately 650°C.
The orthorhombic β-phase can reversibly transfer into the high temperature (HT) crystalline tetragonal α-phase at approximately 1320 ± 20 °C.8,10,11

Besides controlling the Ta2O5 phases by annealing at different temperatures, annealing in different gas atmospheres at elevated temperatures can also be an effective way to tune the stoichiometry of tantalum oxide.8,10 This approach is also often used to further improve the mechanical, electrical, or optical properties of thin films by structural relaxation and stoichiometry change.8,10–12

Altogether, post annealing is an effective way to tune the properties of TaOx-based memristors.8,10,13 For example, annealing a TaOx-based memristor in an oxygen atmosphere at 300 °C can affect the oxygen stoichiometry, which has been found to improve the device endurance.13 Annealing in NH3 at 400 °C, on the other hand, resulted in the incorporation of hydrogen (H) species into TaOx, which improved the device endurance, lowered the forming voltage, and enhanced the retention lifetime of the formed conductive filaments. Besides the effect of annealing on the active TaOx layer, the electrode materials may also be affected by the annealing process. For example, Raman scattering spectra indicated the presence of rutile TiO2 signals in 1 μm thick TiN after annealing in air at 500 °C for 2 h.13

So far, annealing of TaOx-based memristors have been carried out on TaOx films deposited either by sputtering or by atomic layer deposition (ALD). No systematic work on the effect of post-deposition annealing on the resistive switching behavior of TaOx films fabricated by PLD has so far been reported. PLD is a powerful technique for the fabrication of complex oxide while preserving the stoichiometry. In this work, we focus on utilizing post-deposition annealing to tune the stoichiometry and resistive switching behaviors of tantalum oxide-based memristors. By using isochronal annealing steps imposed with controlled heating and cooling, we successfully trigger the switching behavior in devices, which did not show any switching initially. We also reveal the stoichiometry change of TaOx after annealing and propose a possible mechanism for the triggering of the switching behavior.

II. EXPERIMENT

The configuration of the device film stack used in this study was Si/SiO2/TiN/TaOx/W with TiN and W serving as the electrodes and TaOx being the active memristive layer. The substrates are commercially available (100) silicon substrates with 10 ± 10 nm native silicon dioxide, and 100 nm TiN film on top (Prime Wafers), labeled as Si/SiO2/TiN substrates. The TiN layer in the Si/SiO2/TiN substrate acts as the bottom electrode. An active oxide layer of TaOx thin films was deposited by pulsed laser deposition (PLD) through a square-shaped shadow mask in order to expose the TiN bottom electrode. A KrF excimer laser (248 nm, 10 Hz, 4 J/cm2) was used to ablate a commercial ceramic target of Ta2O5 (American Elements) with 99.99% purity and dimensions of 25.4 mm in diameter and 6 mm in thickness. The deposition was carried out keeping the target–substrate distance constant at 7.5 cm. The TaOx thin films were deposited with a thickness of approximately 20 nm at room temperature (RT) with an oxygen pressure P O2 = 2 × 10−3 mbar inside the chamber. The tungsten (W) top electrode layer was deposited by DC magnetron sputtering without intentional substrate heating using the following parameters: 40 sccm Ar gas, 10−3 Torr deposition pressure, 320 V discharge voltage, and 0.2 A discharge current for a deposition time of 300 s. The W top electrodes were patterned into a circular shape with a diameter of 50 μm and a thickness of about 150 nm using an Al2O3 shadow mask.

All electrical tests were carried out using Keithley 4200A with an Imina probe station providing the contact to the W and TiN electrodes through W needle probes. During the two-terminal electrical tests, voltages were applied to the W top electrodes, and the TiN bottom electrodes were grounded. The voltage ramp with 10 mV per step was used in both SET and RESET processes. A compliance current of 1 mA was used in the SET process. The initial resistances of the devices follow a log-normal distribution, which means the log of the initial resistances follow normal distribution. In Fig. 1, the mean values are of the log of the initial resistances and the error bars are the standard deviations of the mean. The electrical conductivity

![Fig. 1](https://via.placeholder.com/150)

**FIG. 1.** (a) Initial resistance distribution for seven as-fabricated samples. Each sample contains 16 devices. The diameter of the top electrodes is 50 μm. The thickness of the TaOx layer is about 20 nm. The inset in (a) shows a schematic illustration of the devices under test and the two-terminal electrical test setups. (b) Change in resistances after annealing at different temperatures. The inset in (b) shows the temperature profile during the annealing process. RS stands for resistive switching. The error bars represent the standard deviation of the mean.
was measured on rectangular-shaped samples \((1 \times 1 \text{ cm}^2)\) in a van der Pauw configuration. A short description of the electrical measurement setup is described in the supplementary material (Figs. S1 and S2).

Chemical and structural changes in the materials induced by the annealing were characterized by x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and energy-dispersive x-ray spectroscopy (EDX). The XPS analyses were performed on an ESCALAB Xi+ x-ray photoelectron spectrometer (Thermo Fisher Scientific, East Grinstead, UK) using a monochromatic Al-Kα x-ray source with a 650 μm spot size and a take-off angle of 90° from the surface plane. A combined ion/electron gun (i.e., a dual-beam source) was used to control sample charging. The pressure in the analysis chamber was \(4 \times 10^{-8} \text{ mbar}\). High resolution local binding energy spectra were obtained for Ta-4f using 20 eV detector pass energy, a dwelling time of 50 ms, and an energy step size of 0.05 eV. The sputter depth profiling was performed on a fraction of the area of \(0.7 \times 0.7 \text{ mm}^2\) with monoatomic Ar⁺ ion beam. The beam has a kinetic energy of 3 KeV, for 10 s each level, and with 30 levels in total. All spectra were shifted according to the O1s spectra peak position using the second O1s spectrum of the as-deposited sample. For the XRD analysis, Bruker D8 Advanced diffractometer (Germany) with Cu Kα \((\lambda = 1.5406 \text{ Å})\) radiation was used. For the STEM analyses, a probe-aberration corrected JEOL JEM-ARM200F microscope equipped with a cold field-emission electron source, a probe Cs-corrector (DCOR, CEOS GmbH), and a large solid-angle JEOL Centurio SDD-type EDX detector was used. STEM imaging and EDX analyses were performed at probe semi-convergence angles of 20 mrad and 28 mrad, resulting in probe sizes of 0.8 Å and 1.0 Å, respectively. Collection angles for high-angle annular dark-field (HAADF) images were 75–310 mrad.

### III. RESULTS AND DISCUSSION

A set of seven samples were fabricated under the same conditions as described in the experimental part. Each sample contains 16 devices defined by a circular W top-electrode with a diameter of 50 μm and a 20 nm active TaOₓ layer. A schematic illustration of the device is shown in the inset of Fig. 1(a). Initially, all devices showed no resistive switching with an average low initial resistance of approximately 5.26 kΩ [Fig. 1(a)]. We annealed the samples at different temperatures ranging from 300 °C to 500 °C in air. Seven annealing temperatures were used: 300 °C, 325 °C, 350 °C, 375 °C, 400 °C, 450 °C, and 500 °C, with a fixed annealing time of 4 h and a ramping rate of 200 °C/h during heating and cooling [inset of Fig. 1(b)]. The resistances after the annealing process at different temperatures are shown in Fig. 1(b). After the annealing process, the ability of the samples to resistive switch was tested at room temperature.

The results of the annealing revealed the following: (1) For annealing temperature smaller than or equal to 300 °C, no resistive switching was observed inside the devices [Figs. 2(a) and 2(b)], (2) from 325 °C to 400 °C, the resistive switching was triggered [Figs. 2(c)–2(f)], and (3) above 400 °C, the average resistance of devices exceeds \(10^{10} \Omega\), showing an insulating state with no resistive switching [Figs. 2(g) and 2(h)]. Typical IV curves and resistance distributions of the switching devices are shown in the supplementary material, Fig. S3.

Thus, only in a limited window, between 325 °C and 400 °C, we could trigger resistive switching behaviors in TiN/TaOₓ/W structured devices. In the following, we, therefore, investigate the underlying origins responsible for enabling the resistive switching within this window and the reasons for terminating the resistive switching when annealed outside this window.

![FIG. 2. Typical IV relation for (a) the as-fabricated devices, and (b)–(h) devices after annealed at 300 °C, 325 °C, 350 °C, 375 °C, 400 °C, 450 °C, and 500 °C, respectively. The dashed lines in (c)–(f) represent the corresponding forming and the first RESET processes.](image-url)
FIG. 3. (a) An illustration of the XPS depth profiling direction. XPS depth profiles of devices (b) as-fabricated, (c) after annealed at 350 °C, and (d) after annealed at 500 °C. The black arrows indicate the etching direction from the surface of TaO$_x$ to the inner part of the TaO$_x$ thin film. The dashed lines represent the binding energy for Ta$^{5+}$.

A. Oxidation and crystallinity of the TaO$_x$ resistive switching layer

In order to understand the oxidation state and the stoichiometry of film and their relation to the resistive switching, we have studied three samples: (1) the as-fabricated sample, (2) the sample annealed at 350 °C, and (3) the sample annealed at 500 °C, by XPS depth profiling (Fig. 3). The black arrows in Fig. 3 represent the XPS depth profile direction from the surface of the TaO$_x$ to the inner part of the TaO$_x$. The depth profiles taken from these samples have a similar analysis time, i.e., approximately a similar depth length.

The spectra were peak fitted using the CasaXPS software. All six oxidation states of Ta, i.e., Ta$^{5+}$, Ta$^{4+}$, Ta$^{3+}$, Ta$^{2+}$, Ta$^{1+}$, and Ta$^0$, were used to build the peak model for fitting. The details of the information of the fitting are given in Table S1 and Fig. S4 in the supplementary material. From the analysis, we can conclude that the TaO$_x$ films contain a mixture of different oxidation states of tantalum. Figure 4 shows the results of the analysis where the O/Ta ratio of the three samples is plotted. As seen from this...
FIG. 5. Resistivity change of TiN and W layers after annealing at different temperatures. The resistivity was tested by using a four-probe van der Pauw configuration on $1 \times 1$ cm$^2$ samples.

At annealing temperatures between $325 \, ^\circ C$ and $400 \, ^\circ C$, a reaction between the TiN and TaO$_x$ takes place leading to the partial oxidation of TiN (TiON) and partial reduction of the TaO$_x$. This corresponds well with the XPS results (Fig. 4) and the resistive switching shown in Figs. 1 and 2. However, we cannot exclude that part of the contribution to the resistive switching might come from the possible formation of the TiON phase. In other words, the resistive switching depends on the right amount of oxygen vacancies in the device. Typical $I/V$ curves of TiN/TaO$_x$/W devices with TaO$_x$ deposited at different oxygen pressures, i.e., different oxygen vacancies, are shown in the supplementary material as Fig. S5.

Note that after being annealed at $500 \, ^\circ C$, the devices were non-switchable due to the oxidation of the TaO$_x$ as well as the TiN bottom electrode, which is supported by the electrical measurement in Fig. 5 showing that the samples are insulating. This will be discussed in detail in the following paragraph.

Based on the XRD analysis (supplementary material, Fig. S6), up to $400 \, ^\circ C$, the TaO$_x$ films were all amorphous, as indicated also with the grazing incidence x-ray diffraction (GIXD) experiments [Figs. S6(b)–S6(d)]. For annealing temperature above $400 \, ^\circ C$, the amorphous TaO$_x$ crystallizes into a low-temperature $\beta$-phase at elevated temperatures between $500 \, ^\circ C$ to $700 \, ^\circ C$. The ordering process of the amorphous TaO$_x$ induced by thermal annealing is a slow process and hardly gets completed even at $700 \, ^\circ C$.

B. The effect of electrodes and interfaces

Another source of the possible absence of resistive switching is the degradation of the electrodes during annealing. Besides the oxidation process of TaO$_x$, we also observe an indication of oxidation of the TiN electrode materials, i.e., from the transport measurements. After the annealing process (on samples similar to the one shown in Fig. 3), the resistivity of both the TiN bottom electrode layer and the W top electrode layer was tested using a four-probe van der Pauw configuration. The four-probe test was

FIG. 6. (a) Resistance change of the TiN/TaO$_x$/W and TiN/W/TaO$_x$/W structured devices after the annealing process. (b) Typical $I/V$ curves for TiN/W/TaO$_x$/W structured devices.
carried out on the TiN layer of the devices, and on a new set of samples only consisting of bare W electrode. All tests were carried out at room temperature after the annealing process. The resistivity of the TiN layers shows an increase from 320 ± 19 μΩ cm without any post-annealing process to 592 ± 61 μΩ cm after being annealed at 400 °C. As the annealing temperatures increased above 400 °C, the TiN layer became very insulating with a resistivity above the detection limit of our equipment (Fig. 5). On the other hand, the W layer kept a stable resistivity even after being annealed at 500 °C.

In addition to the stoichiometry of the TaOₓ layer, one needs also to ensure the right choice of the electrode combination, which is also a crucial factor for the resistive switching. By inserting a layer of W between the TiN and the TaOₓ (Si/SiO₂/TiN/W/TaOₓ/W), as a “blocking” layer for oxygen, the resistance increased from 10²Ω to 10⁷Ω, see Fig. 6(a). However, no resistive switching was observed in these samples [Fig. 6(b)]. The devices showed an Ohmic IV relationship for the annealing temperature up to 400 °C. Devices after being annealed at 500 °C showed a forming/SET process but cannot be switched back to the high resistance state at the negative voltage side.

In order to understand the influence of annealing on the interface profiles, detailed STEM investigations were carried out on similar TiN/TaOₓ/W samples (Fig. 3). Figures 7(a)–7(c) show STEM-HAADF images of the layered structure overlapped by the EDX scans. From STEM-EDX chemical investigations, it is clear that the out-of-plane elemental intermixing at both interfaces, TiN/TaOₓ and TaOₓ/W, is present. The as-fabricated sample [Fig. 7(a)] shows no indication of clear intermixing, although there might be intermixing only at a very narrow interval close to the interface (∼5 nm). For sample annealed at 325 °C [Fig. 7(b)], the STEM EDX indicates that there is a diffusion of Ta into the W layer, while the W does not seem to diffuse into the TaOₓ layer (see also Fig. S7). After annealing at 500 °C [Fig. 7(c)], we observe the diffusion of W into the TaOₓ as well as the diffusion of Ta into the W layer. Additionally, we have observed a diffusion of both Ta and O into the TiN layer. This supports our XPS and the electrical measurements indicating that the TiN is probably partially oxidized at 500 °C.

IV. CONCLUSION

In this work, we were able to trigger the resistive switching in TiN/TaOₓ/W devices by applying a post-annealing procedure. We identify three different temperature regimes.

- **T ≤ 300 °C**: The devices are thermally stable when exposed to annealing in air up to 300 °C for 4 h. With the given deposition parameters used for the TaOₓ deposition, no resistive switching was observed at room temperature.
- **300 °C < T ≤ 400 °C**: The devices showed resistive switching after annealing within this temperature window. As indicated by the XPS depth profiling, in this temperature range, the TaOₓ layer reduces while the TiN is oxidized. In this temperature range, both the non-stoichiometry of TaOₓ and oxidation/reduction at the TaOₓ/electrode interface played an essential role in triggering resistive switching.
- **T > 400 °C**: We observed insulating films. This happened due to the oxidation of the TiN bottom electrode and the shift of the TaOₓ to the more stoichiometric composition.
We have shown that post-annealing can enable resistive switching and allow studying the switching behavior in samples, which otherwise did not show resistive switching. Annealing can be a simple yet powerful method for triggering the resistive switching. By post-annealing the devices in a temperature range between 325 °C and 400 °C, the initial resistances of the TiN/TaO\textsubscript{x}/W structured devices increased from 10\textsuperscript{3} Ω to 10\textsuperscript{6} Ω resulting in the resistive switching. The temperature range observed in these experiments related to the stability of the electrodes and the active layer. Both the stoichiometric TaO\textsubscript{x} layer and the TiN/TaO\textsubscript{x} interface or the TiN electrode played an important role in the emergence of resistive switching behavior.

**SUPPLEMENTARY MATERIAL**

See the supplementary material for more information about the electrical test set-ups, the typical I-V curves and resistances of switchable devices, the XPS fitting details, the XRD spectra of TaO\textsubscript{x} materials, and the supplementary information about EDX elemental profile.

**ACKNOWLEDGMENTS**

The authors acknowledge Julia Deuschle for FIB lamella preparation. Y. Eren Suyolcu and Peter A. van Aken acknowledge funding from the European Union’s Horizon 2020 research and innovation program under Grant Agreement No. 823717–ESTEEM3. The authors thank the support from the Independent Research Fund Denmark, Grant No. 6111-00145B.

The authors declare no conflict of interest.

**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**REFERENCES**


