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# Influence of radiation on titanium dioxide memristors

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**Abstract:** Effects of titanium dioxide memristor exposure to proton and ion beams are investigated. A memristor model assuming ohmic electronic conduction and linear ionic drift is used for the analysis. Simulations of particle transport suggest that radiation induced oxygen ion/oxygen vacancy pairs can influence the device's operation by lowering both the mobility of the vacancies and the resistance of the stoichiometric oxide region. These radiation induced changes affect the current-voltage characteristic and state retention ability of the memristor

**Keywords:** Memristor, titanium dioxide, protons, ions, Monte Carlo method

## 1 Introduction

Memristor is a one-port circuit element that maintains a nonlinear relationship between time integrals of the voltage across its terminals and the current running through it. In mathematical terms, this defining property of a memristor can be expressed in a differential form as:

$$v(t) = M(w)i(t) \tag{1}$$

where M is called *memristance*, and w is a state variable that, in turn, depends on the time integral of the current, i.e. on the amount of charge $q$ that has passed through the device. It is from this nonlinear relationship that the characteristic properties of memristors ensue: the hysteretic features of the $i-v$ curve (namely the single and double loops, with segments of apperent negative differential resistance) and the ability to operate as a switch by holding or "remembering" the value of resistance (which gives memristor its name, as a portmanteau for "memory resistor"). Since, in general, there are many ways for such a nonlinear relationship to hold, there is no such thing as a generic memristor. The nonlinearity can in principal be achieved through quantities (state variables) specific of each separate realization of the memristor.

Equation (1) suggests that memristance can be regarded as the *effective resistance* of a memristor. Furthermore, a memristor does not introduce a phase shift between current and

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voltage at zero crossings, i.e. $i = 0$ if and only if $v = 0$. It is therefore a purely dissipative element, much like the resistor. In the trivial case of constant $M$, when nonlinearity is removed, memristor indeed reduces to a resistor. The physical unit for memristance is Ohm.

In the nontrivial case of $M$ depending on $q$ via $w$, memristor has such an $i-v$ curve that no combination of nonlinear resistors, capacitors or inductors can reproduce. This inability to duplicate the properties of a memristor with the other passive circuit elements is what lead to it being seen as the forth fundamental passive two-terminal circuit element, when it was first hypothesized back in 1971 [1].

A memristor can remember a state by freezing the value of the state variable $w$, which is not necessarily zero when $v = 0$. The value of $w$ at this point depends on the history of the voltage change, i.e. on the shape, amplitude and frequency of the driving voltage.

A physical component demonstrating memristance was not created until 2008, when a two-terminal (one-port) realization of a memristor, based on a thin film of titanium dioxide, was finally constructed by the Hewlett-Packard Laboratories [2]. Operation of this device relies on the distribution of oxygen vacancies in the oxide, which can be perturbed through atom displacement interactions when the component is exposed to proton or ion beams.

## 2 The titanium dioxide memristor

The constructed memristor is composed of a titanium dioxide thin film between two platinum electrodes. The oxide layer further consists of a high-resistance stoichiometric $TiO_2$ layer and a low-resistance oxygen deficient $TiO_{2-x}$ layer, in which oxygen vacancies serve as electron donors. Even a small nonstoichiometry of 0.1% in $TiO_{2-x}$ is equivalent to $5 \cdot 10^{19}$ donors/cm$^3$ and has a very strong effect on the electronic conductivity. Memristance is achieved in this stacked $TiO_2 - TiO_{2-x}$ structure through a specific coupling of electronic and ionic transport. Oxygen vacancies act as mobile +2-charged ions, which can drift in the electric field created by a voltage applied to the device's terminals, shifting the boundary between the high-resistance and low-resistance layers. The charge-flow dependent state variable is the thickness w of the conducting oxygen-poor layer.

Since the concentration of oxygen vacancies in the $TiO_{2-x}$ region is large, the transfer of some of the vacancies into the stoichiometric layer has very little effect on the electronic conductivity of the oxygen-poor region. On the other hand, the electronic conductivity of the initially stoichiometric material increases dramatically, since it is going from a state in which there are no vacancies to the one in which there are some.

The conduction mechanism in the titanium dioxide memristor involves electrons from the electrodes tunneling through the energy barrier existing at the $TiO_2$/metal electrode interface. Both the height and the width of the tunnel barrier are dependent on the size of the oxygen deficient region within the memristor, diminishing as w becomes larger. Migration of oxygen vacancies, on the other hand, is best described as weak ionic conduction in a solid [3]. The coupling of these two drifts rests on the fact that both charged species involved in memristor operation (electrons and oxygen vacancies) move by virtue of the same electric field present across the low-resistance region [4].

An idealized physical model of the titanium dioxide memristor used in this paper assumes ohmic electronic conduction and linear ionic drift. Total resistance of the device is determined as a series connection of the highly resistive stoichiometric layer and the conducting oxygen-poor layer. Ohm's law relation between voltage and current is then:

$$v(t) = \left( R_{ON}\frac{w(t)}{D} + R_{OFF}\left(1 - \frac{w(t)}{D}\right)\right) i(t) \tag{2}$$

where $w(t)$ is the size of the oxygen-poor layer, while $R_{ON}$ and $R_{OFF}$ are the resistances of the oxygen-poor and the stoichiometric region respectfully, given for the full length D of the device. Based on the said assumptions, the following expression for doped region size is obtained:

$$w(t) = w_0 + \frac{\mu_{OV}R_{ON}}{D}\int_0^t i(\tau)d\tau = w_0 + \frac{\mu_{OV}R_{ON}}{D}q(t) \tag{3}$$

where $w(t=0) = w_0$ is the initial size of the oxygen deficient region, $\mu_{OV}$ is the mobility of oxygen vacancies in titanium dioxide, and $q(t)$ is the electronic charge that has passed through the device, for which $q(t=0) = 0$. Inserting equation (3) into equation (2), and comparing it to equation (1), memristance is obtained as:

$$M(q) = R_0 - \Delta R\frac{\mu_{OV}R_{ON}}{D^2}q(t) \tag{4}$$

where $R_0 = R_{ON}(w_0/D) + R_{OFF}(1 - w_0/D)$ is the effective resistance at $t = 0$, and $\Delta R = R_{OFF} - R_{ON}$. Memristance is thus dependent directly only on the charge which has passed through the memristor. If the applied voltage is removed, the memristor "remembers" its last state, i.e. the value of total resistance at the moment of voltage suspension [2].

Since the mobility of oxygen vacancies in titanium dioxide is low ($\mu_{OV} \sim 10^{-10}cm^2V^{-1}s^{-1}$), memristive effects are appreciable only when the memristor size is nano-scale, which is illustrated by the inverse-square dependence on total film thickness ($M \sim 1/D^2$) in equation (4). Only in a film this thin is the amount of time required to drift enough oxygen vacancies into or out of the $TiO_2$ region to substantially change its conductivity short enough. Moreover, for a given $D$, memristive behaviour is expressed only when $\Delta R >> R0$.

Equation (1) can now be rewritten as:

$$v(t) = M(q)\frac{dq}{dt} \tag{5}$$

Inserting equation (4) into equation (5), solving for $q(t)$ and substituting it back in (5), yields the $i - v$ characteristic of an ideal titanium dioxide memristor:

$$i(t) = \frac{v(t)}{R_0\sqrt{1 \mp 2\Delta R\frac{\mu_{OV}R_{ON}}{D^2R_0^2}\int_0^t v(\tau)d\tau}} \tag{6}$$

The minus sign in the denominator of equation (6) applies when the oxygen-poor region is expanding, while the plus sign corresponds to the shrinking of this region.

Typical memristor $i-v$ curve for a sinusoidal driving voltage, obtained theoretically from equation (6) as a 2D parametric plot, is shown in Fig. 1. It has a form of a double-loop hysteresis, with segments of negative differential resistance corresponding to the intervals during which $w(t)$ is increasing while $v(t)$ is already in recess, but still of same polarity. A similar hysteresis is obtained for any symmetrical ac voltage applied to the memristor. The hysteresis is observed only for small-amplitude ($\sim$ 1V) low-frequency ($\sim$ 1Hz) voltages, for which w never reaches either of the limiting values (0 or $D$), i.e. the low resistance oxygen-poor layer never stretches across the length of the device, nor vanishes completely. For high-frequency low-amplitude ac voltages, the size of the oxygen-deficient layer barely changes for the duration of the voltage half-period, making the effective resistance of the memristor nearly constant and reducing the $i-v$ hysteresis to a straight line, which is also demonstrated in Fig. 1.

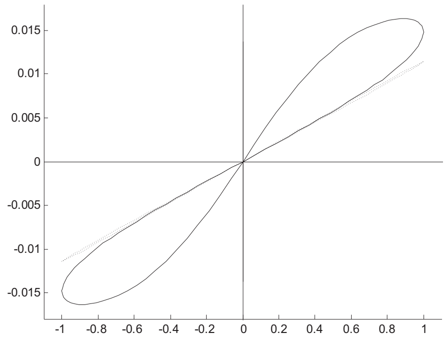



Fig. 1. Current-voltage characteristic of a titanium dioxide memristor, for which ohmic electronic conduction and linear ionic drift of oxygen vacancies are assumed. The applied voltage is $v(t) = v_0 \sin(\omega t)$, with $v_0 = 1$V and $\omega = \pi/1os^{-1}$. Other parameters are: $R_{ON} = 100\Omega$, $R_{OFF} = 16k\Omega$, $D = 60$ nm, $w_0 = 30$ nm, $\mu_{OV} = 10^{-10}cm^2s^{-1}V^{-1}$. The dotted plot is for a ten-time higher frequency of the sinusoidal voltage.

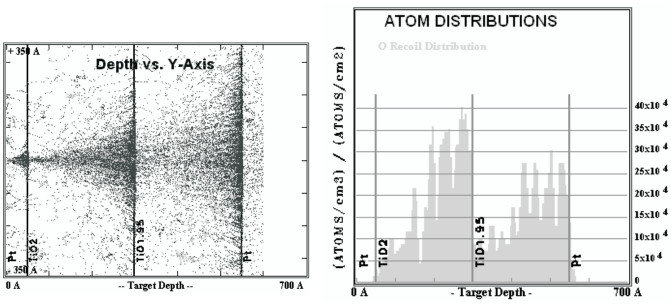
If $w$ reaches either of the two boundaries, it remains constant until the voltage polarity is reversed. When boundary conditions such as these are introduced, the device is more appropriately referred to as a memristive system, that acts as a true memristor, one for which equation (6) holds, only as long as $w$ is within the interval $(0,D)$ [5]. The value of $w$ can be pushed to one of the limits either by large applied voltages or by long times under same polarity bias. Boundary states differ greatly in resistance, thus forming the basis of memristor bipolar switching. If the voltage across memristor terminals is suddenly suspended, the value of memristance is frozen and stays unchanged while there is no bias. Long state lifetimes and fast switching observed in titanium dioxide memristors make them potential candidates for future non-volatile RRAMs (Resistive Random-Access Memories), based on the so called crossbar architecture.

This paper examines the influence of proton and ion beam irradiation on the shape of the titanium dioxide memristor $i-v$ hysteresis, and on state retention when memristor is used as a switch.

## 3 Results of radiation transport simulation

Monte Carlo simulations of proton and ion beams traversing the Pt-$TiO_2$-$TiO_{2-x-}$Pt structure were performed in the TRIM part of the SRIM software package [6].

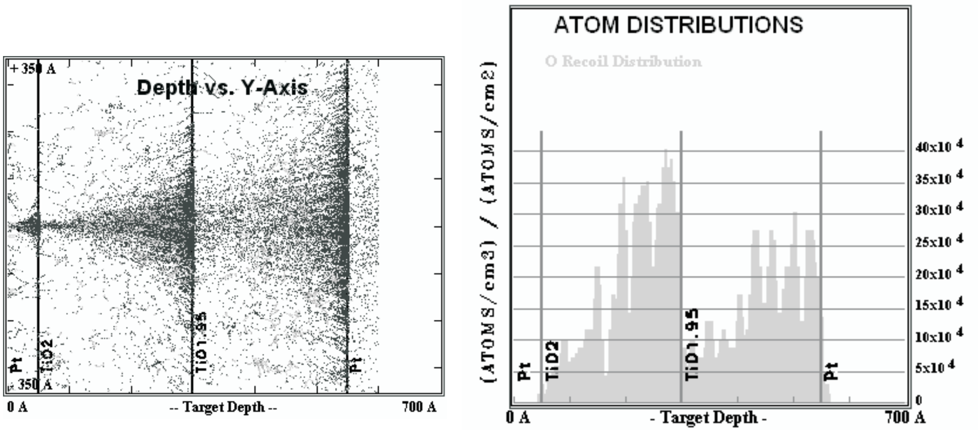
Fig. 2 a) shows the trajectories of one thousand 10 keV protons traversing the 60 nm thick memristor structure. The incident proton beam is perpendicular to the surface of the left platinum electrode. The thicknesses of the layers along the horizontal axis are as follows: 5 nm platinum layer, 25 nm stoichiometric $TiO_2$ layer, 25 nm oxygen deficient $TiO_{2-x}$ layer ($x = 0.05$), and another 5 nm platinum layer. Total length of the titanium dioxide film is then $D = 50$ nm. Fig. 2 b) presents the distribution of oxygen ions displaced by the impinging protons. The default value of oxygen atom threshold displacement energy in titanium dioxide provided by SRIM was changed to a value obtained by a molecular dynamics simulation study for the rutile modification of $TiO_2$ [7].




a) b)

Fig. 2. Simulation results for a 10 keV proton beam (1000 protons) incident perpendicularly on a Pt-$TiO_2$-$TiO_{2-x-}$Pt stack, with the total thickness of 60 nm. a) Particle and ion tracks. b) Distribution of displaced oxygen atoms. Target depth axis is in units of angstrom.

Fig. 3 provides an example of a 10 keV carbon ion beam traversing the same memristor structure, with equal thicknesses of the $TiO_2$ and the $TiO_{1.95}$ layer.




a) b)

Fig. 3. Simulation results for a 10 keV carbon ion beam (100 ions) incident perpendicularly on a stacked $Pt - TiO_2 - TiO_{2-x-}Pt$ structure, with the total thickness of 60 nm. a) Ion tracks. b) Distribution of displaced oxygen atoms. Target depth axis is in units of angstrom.

## 4 Discussion

As Monte Carlo simulations of proton and ion transport show, these radiations can cause the generation of a significant amount of oxygen ion/oxygen vacancy pairs in both the high- and the low-resistance layers of titanium dioxide. Whereas the electronic conductivity of the low-resistance oxygen-poor region is little affected by the appearance of additional vacancies, the effect on the conductance of the stoichiometric vacancy-free $TiO_2$ region can be considerable. Radiation induced emergence of oxygen vacancies in the stoichiometric region can cause its resistance $R_{OFF}$ to drop, disrupting the $R_{OFF}/R_{ON}$ ratio of the memristor. The change of the resistance ratio affects the memristor $i - v$ characteristic, through quantities $R_0$ and $\Delta R$ in equation (6). The effect that the decrease of $R_{OFF}$ has on the memristor $i - v$ curve is illustrated in Fig. 4.

Oxygen ions $O^{2-}$ produced by radiation in the stoichiometric layer can become interstitial atoms, or migrate in the electric field. If the amplitude of the applied voltage is high enough, oxygen ions may reach one of the electrodes, where they can form $O_2$ gas and cause deformation of the oxide/metal interface, leading to permanent disruption of memristor operation [8]. While traversing the oxygen-deficient layer, some oxygen ions may recombine with the existing vacancies. The presence of oxygen ions and atoms can also reduce the mobility of oxygen vacancies $\mu_{OV}$ [9]. According to equation (6), a decrease of $\mu_{OV}$ affects the memristor $i - v$ hysteresis, as shown by example plots in Fig. 5.

The specific switching functionality of a memristor rests on a high $R_{OFF}/R_{ON}$ ratio, which enables two boundary states to be unambiguously distinguishable by a read voltage signal, and on the ability to hold a state at zero bias. Since for the highly conducting boundary state, corresponding to $w = D$, the low-resistance region stretches across the whole of

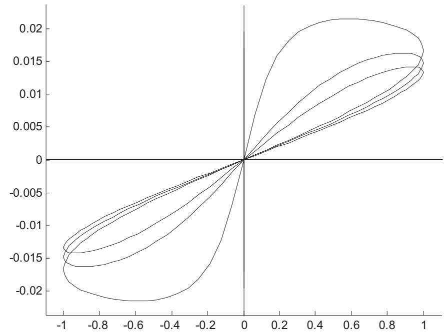



Fig. 4. Current-voltage curves of a titanium dioxide memristor, plotted for three different values of the stoichiometric region resistance: $R_{OFF} = 18k\Omega, 16k\Omega$, and $14k\Omega$. The applied sinusoidal voltage and all other parameters are the same as for Fig. 1. The decrease in $R_{OFF}$ is caused by radiation induced emergence of oxygen vacancies in the stoichiometric $TiO_2$ region.

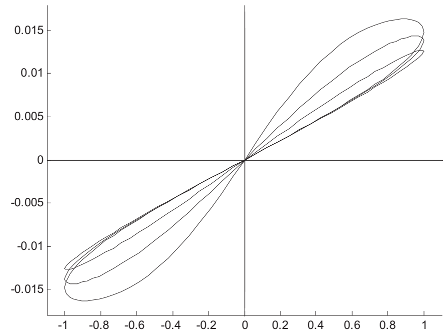



Fig. 5. Current-voltage curves of a titanium dioxide memristor, plotted for three different values of the oxygen vacancy mobility: $\mu_{OV1} = 10^{-10}$ $cm^2s^{-1}V^{-1}$, $\mu_{OV2} = 0.8 \cdot 10^{-10}$ $cm^2s^{-1}V^{-1}$, and $\mu_{OV3} = 0.5 \cdot 10^{-10}$ $cm^2s^{-1}V^{-1}$. The applied sinusoidal voltage and all other parameters are the same as for Fig. 1. The decrease in $\mu_{OV}$ is caused by the radiation induced presence of oxygen ions and atoms in the oxide.

the oxide, the radiation produced change of $R_{OFF}$ has no effect on state retention. The high-total-resistance state is, however, susceptible to change when exposed to proton or ion radiation. This state, corresponding to $w \approx 0$, is characterized by a diminished or non-existant oxygen-poor region, with the total memristor resistance approximately equal to $R_{OFF}$. The decrease of $R_{OFF}$ caused by irradiation can therefore perturb this state, resulting in an error at readout.

## 5 Conclusion

Exposure of a titanium dioxide memristor to proton and ion beams can influence the device's operation in several ways. Significant generation of oxygen ion/oxygen vacancy pairs in the oxide is to be expected, as suggested by Monte Carlo simulations of particle transport. Radiation induced appearance of oxygen vacancies in the stoichiometric TiO2 layer can cause its resistance to drop, producing counter-clockwise rotation of the memristor $i - v$ curve and a larger swing in its double-loops. The presence of oxygen ions and atoms displaced by the radiation can reduce the mobility of oxygen vacancies, causing the memristor i-v curve to rotate clockwise. When memristor is operated as a switching element of a non-volatile memory, e.g. within a crossbar array, the high-total-resistance state, characterized by a diminished oxygen-poor region, can be perturbed by irradiation and result in an erroneous readout. Finally, if the displaced oxygen ions reach the platinum electrodes, they can form $O_2$ gas and cause permanent disruption of memristor functionality.

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