Simulation-based Comparison of Energy Deposition Pathways in Neutron-irradiated TiO_2 Memristors

Milan Vujović, Slobodan Milutinović, Miloš Vujisić

***Abstract*—Neutron irradiation of titanium oxide memristors is studied through Monte Carlo simulations of neutron transport. Separate software packages are utilized for registering primary knock-on atom distribution, resulting from incident neutrons, and subsequent energy deposition of these displaced ions. Energy deposition mechanisms for secondary ions are compared at various incident neutron energies. Ranges of neutron energy for which radiation-induced changes in the oxide layer are expected to cause greatest alterations of memristor functionality are identified and linked to energy deposition pathways.**

***Index Terms* — Neutrons; memristors; titanium dioxide, Monte Carlo simulation.**

I. Introduction

MEMRISTORS are a promising new kind of electrical component. Predicted within nonlinear electrical circuit theory over 45 years ago, they started being produced only relatively recently, with the advent of nanotechnology [1,2]. Memristor is a passive two-terminal electrical component that maintains a nonlinear relationship between time integrals of the voltage across its terminals and the current running through it [2-4]. This nonlinear relationship gives memristors some distinct properties: the pinched hysteretic current-voltage (*i-v*) curve and the ability to operate as a switch by holding or "remembering" the value of resistance (which is where the name comes from, an abbreviation for "memory resistor"). When the electric power supply to a memristor is turned off, it remembers its most recent value of resistance, until power is turned on again. Memristor resistance (known as *memristance*) depends on how much electric charge has previously flown through the component and in which direction. Envisaged applications of memristors include nanoelectronic memories, computer logic components and neuro-memristive computer architectures.

Since, in general, there are many ways for the nonlinear relationship between current and voltage to hold, there is no such thing as a generic memristor. Among the many physical realizations of memristors, those based on metal-oxides, and especially on titanium dioxide, have garnered much attention in recent scientific research.

Wider use of memories and electronic devices containing TiO_2 memristors will require them to operate in various environments. Some applications will include exposure of memristors to ionizing radiation fields, from cosmic rays in space applications to neutrons at nuclear reactors.

Previous studies of radiation effects in oxide-based memristors focused more on the damage caused by charged particles traversing the memristor. Monte Carlo simulations have indicated that exposure of memristors to beams of protons, alpha particles or heavy ions can give rise to changes in oxygen vacancy concentration and influence memristor's operation [4,5]. Experiments which conducted actual irradiations of oxide-based memristors with several ion species have confirmed the changes in *i-v* curves predicted by the simulations, but observed only moderate change in the switching characteristics of the tested devices [6,7].

Neutron irradiation of oxide-based memristors, on the other hand, has by no means been researched extensively. Expanding upon previous research [8], we have investigated and compared energy deposition pathways of neutrons in the TiO_2 memristor stack. Using Monte Carlo simulations of neutron transport, we've been able to vary neutron energy across a wide range of values, from 10 keV to 1 MeV, focusing on the damage produced by neutron collisions in the active volume of the TiO_2 memristor, i.e. in the oxide double-layer.

II. Simulation Setup

A. Device and Source Models

A single titanium oxide memristor was modeled as a multi-layered structure with a quadratic 5μm × 5μm base (Fig. 1), consisting of (bottom to top): a 250 μm thick SiO_2 substrate, 5 nm thick titanium layer, 15 nm thick platinum electrode, 26 nm thick titanium oxide and another platinum electrode over it, 31 nm in thickness. The oxide, placed between two platinum electrodes, was further subdivided into two layers, one of which was stoichiometric (TiO_2) and the other oxygen-depleted ($TiO_{1.95}$), consistent with the actual structure of a memristor of this kind [2]. The two oxide layers were of equal thickness, 13 nm each. Although the dimensions of these

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layers change when memristor is operated in ac mode, and one of the two logic states (corresponding to one of the layers encompassing the whole of the oxide) was shown to be more radiation sensitive [4], we have chosen equal layer dimensions because one of the goals was to check if there would be any difference in vacancy production or energy deposition depending on the stoichiometry only, regardless of layer volume.

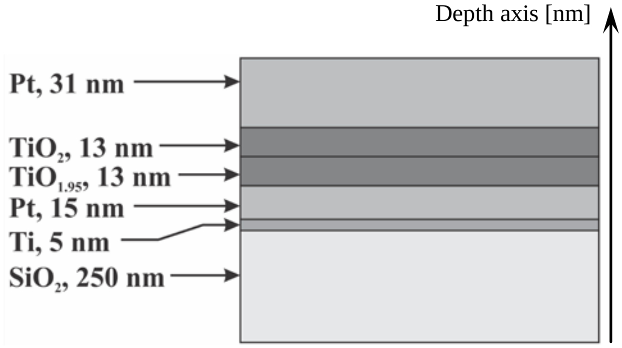


Fig. 1. Geometry of TiO_2 memristor model used for MCNP5 and TRIM simulations.

Isotropic irradiation of the memristor was modeled by a neutron source shaped as a thin spherical shell, 15 µm in diameter, encircling the memristor and centered around the midpoint of the oxide, which is at the center of the $TiO_2/TiO_{1.95}$ interface. The inside of the hollow spherical neutron source was filled with air, i.e. the medium surrounding the memristor was air.

B. Modeling Particle Interactions and Energy Deposition

In order to achieve higher interaction efficiency, monoenergetic neutrons emitted from uniformly sampled points at the spherical surface were all directed inwards, towards the center of the sphere. Each simulation run was performed at another neutron energy in the 0.01−1 MeV range, and followed 10^9 neutron histories.

Two separate software packages were utilized for Monte Carlo simulations of neutrons and charged secondaries produced in neutron interactions. Neutron transport was simulated in MCNP5, while transport of titanium and oxygen ions, displaced by incident neutrons in the oxide double-layer, was simulated in SRIM. MCNP is a general-purpose Monte Carlo code that can be used for neutron, photon, electron, or coupled neutron/photon/electron transport [9]. TRIM part of the SRIM software package performs Monte Carlo simulations of heavy charged particle and ion interactions in matter, based on binary collisions governed by the Ziegler, Biersack and Littmark (ZBL) potential [10].

In order to use TRIM for determining the final number of defects in TiO_2 memristor resulting from neutron interactions with titanium and oxygen atoms, as well as energy deposition profiles in the oxide, TRIM.DAT input file had to be prepared from MCNP5 outputs. Data needed for TRIM.DAT included struck atom energy, initial position, and direction cosines for each and every primary knock-on atom (PKA), i.e. for each atom in the oxide struck directly by a neutron and displaced from its site. These information were obtained from PTRAC files, which are created as outputs by MCNP5 runs. Based on conservation of momentum and using the extracted data, characteristics of each PKA (atomic number, energy, position and direction) were determined and prepared in standard format required by the TRIM.DAT input file.

Both MCNP5 and TRIM codes used the same memristor model and geometry, described in the previous section. Registration of coordinate systems and memristor stack placement between the two codes was somewhat of a challenge.

Following [11], TRIM output files IONIZ.txt and VACANCY.txt were then used to obtain profiles of non-ionizing energy loss (NIEL), linear energy transfer (LET), and vacancy production across the memristor stack.

III. Simulation Results and Discussion

Coupled Monte Carlo simulations of neutron and secondary ion transport show that oxygen ion/oxygen vacancy pairs are generated in both the stoichiometric and the oxygen-depleted layer of titanium dioxide. Titanium atom displacements also occur throughout the oxide. Primary displaced (knock-on) titanium and oxygen atoms cause further atomic displacements, and also deposit energy through interactions with atomic electrons. These two pathways of energy deposition (i.e. non-ionizing and ionizing) are reflected in NIEL and LET profiles, respectively.

Number of titanium and oxygen PKAs in each of the two oxide layers at every neutron energy used in simulations is presented in Table 1.

TABLE 1. Number of PKAs Generated by Neutrons of Different Energies in Both Oxide Layers of the TiO_2 Memristor.

Neutron energy [MeV]	Number of titanium PKAs	Number of oxygen PKAs
TiO_2 layer		
0.01	7385	2259
0.0178	33069	2240
0.05	1382	2170
0.1	1311	2119
0.435	533	9829
0.5	726	2668
1	1164	4833
$TiO_{1.95}$ layer		
0.01	7362	2254
0.0178	33290	2189
0.05	1310	2198
0.1	1245	2131
0.435	477	9603
0.5	679	2637
1	1067	4743

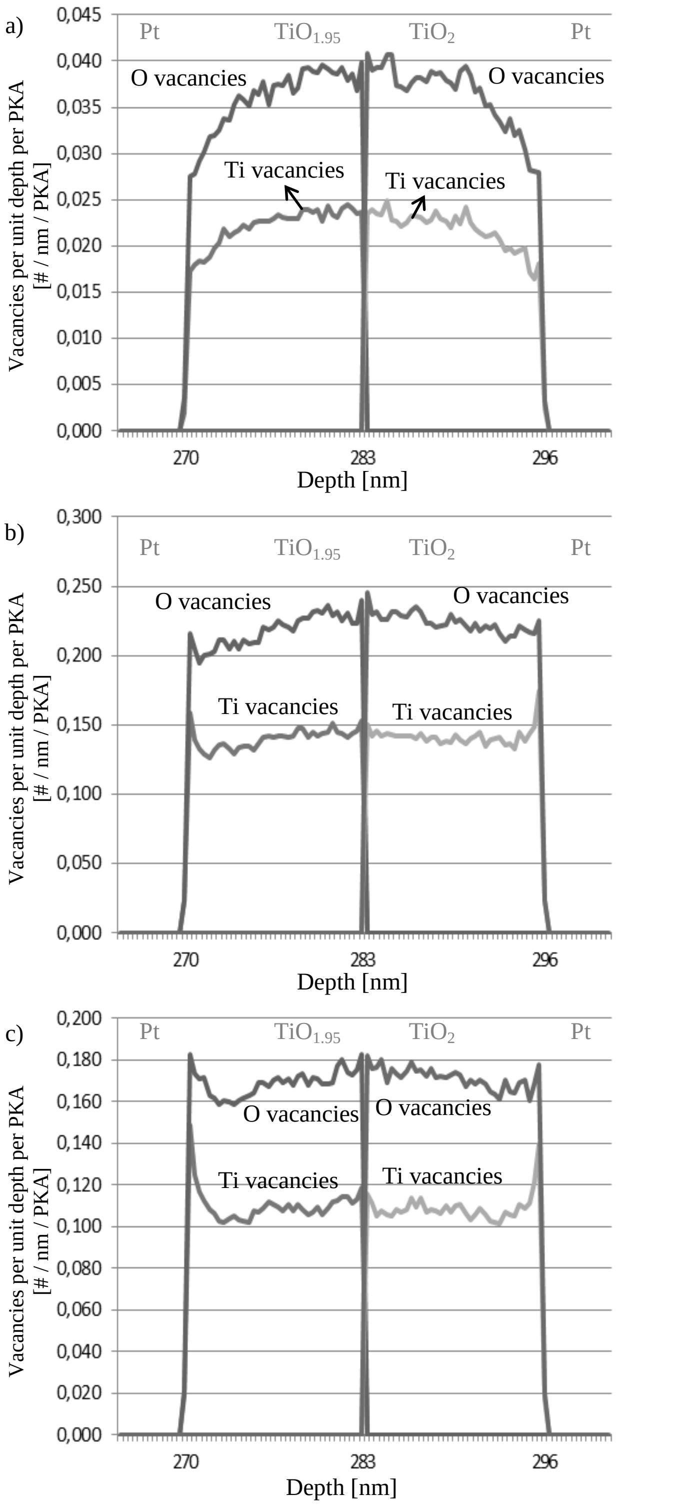


Fig. 2. Vacancy production profiles across the oxide double-layer in the TiO_2 memristor for neutron energies of a) 0.01 MeV, b) 0.5 MeV and c) 1 MeV.

Two out of seven neutron energies were chosen at the resonances in neutron elastic scattering cross-sections. At 0.0178 MeV there is a resonance peak for neutron elastic scattering from ^{48}Ti, and at 0.435 MeV from ^{16}O.

Vacancy profiles across the oxide double-layer in the TiO_2 memristor are shown in Fig. 2 for three neutron energies (0.01, 0.5 and 1 MeV). Distribution of both titanium and oxygen vacancies becomes more uniform across the oxide as neutron energy rises. There is a slight decrease in vacancy production as neutron energy goes into the MeV range, as observed in plots b) and c) of Fig. 2. Oxygen vacancies appear in higher concentrations than titanium ones. More oxygen vacancies are produced in the stoichiometric than in the oxygen-depleted layer. Whereas the conductivity of the low-resistance oxygen-depleted layer ($TiO_{1.95}$) is little affected by the appearance of additional vacancies, the effect on the conductivity of the stoichiometric vacancy-free region (TiO_2) can be considerable, which can lead to significant changes in memristor's *i-v* curve.

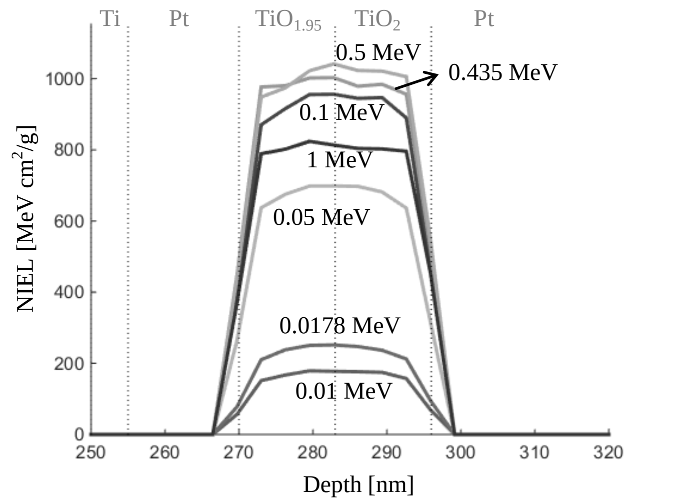


Fig. 3. Mass non-ionizing energy loss (NIEL/ρ) profiles in the oxide double-layer at all seven neutron energies used in simulations.

Profiles of mass non-ionizing energy loss (NIEL divided by material density) and mass LET across the oxide double-layer at all seven neutron energies used in simulations are shown in Figs. 3 and 4, respectively.

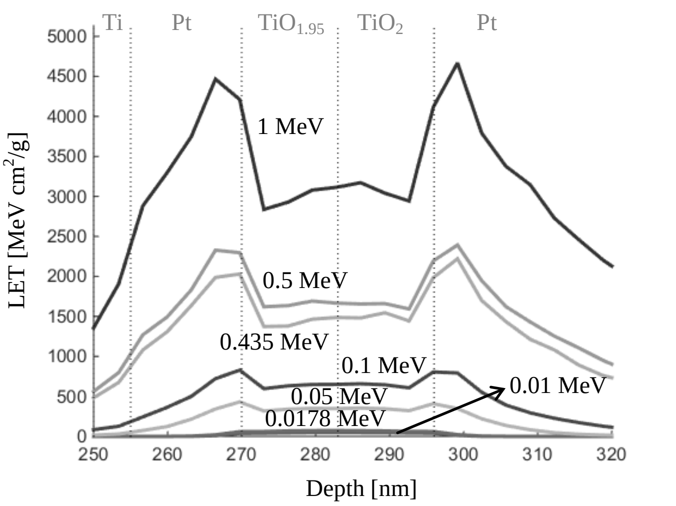
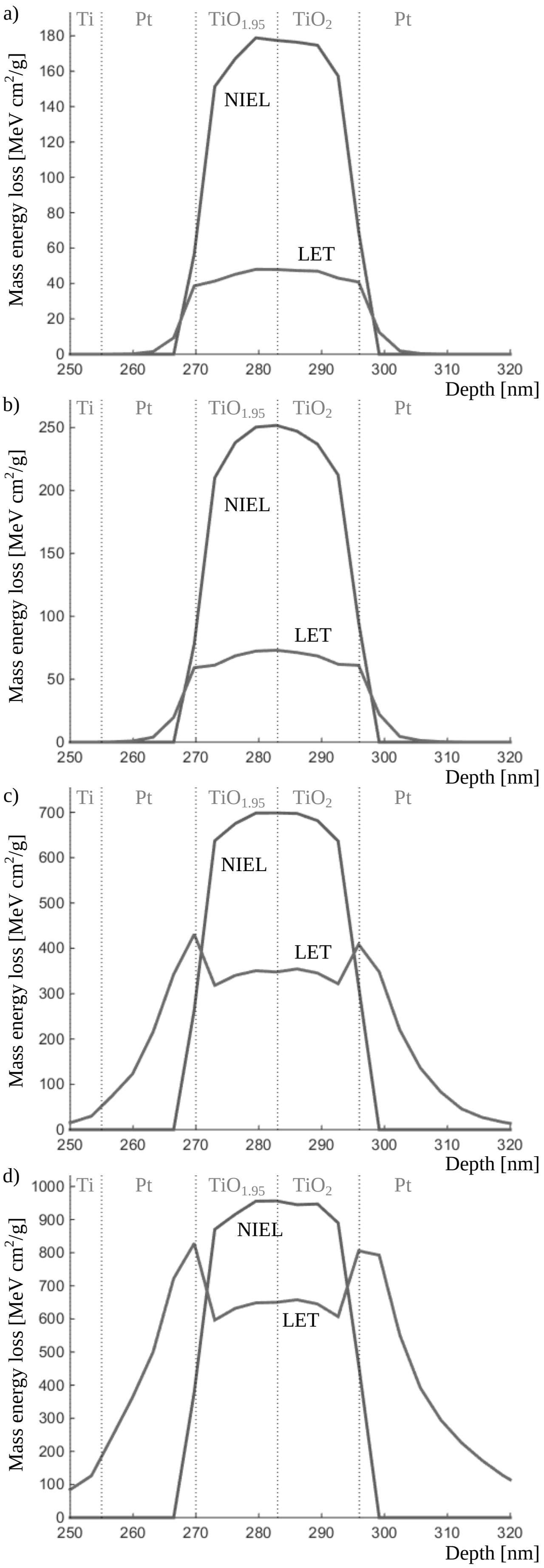


Fig. 4. Mass linear energy transfer (LET/ρ) profiles in the oxide double-layer at all seven neutron energies used in simulations.



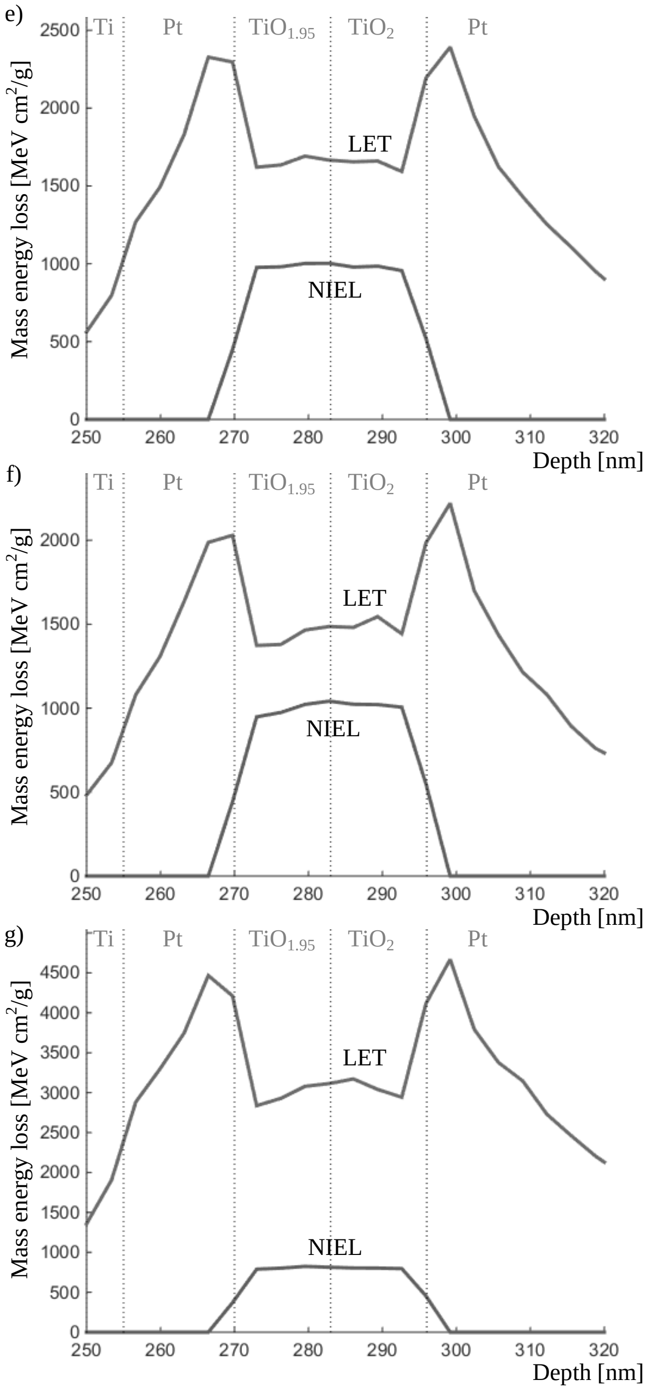


Fig. 5. Mass NIEL and LET profiles in the oxide stack at all seven neutron energies used in simulations: a) 0.01 MeV, b) 0.0178 MeV, c) 0.05 MeV, d) 0.1 MeV, e) 0.435 MeV, f) 0.5 MeV and g) 1 MeV.

NIEL and LET profiles are shown again in Fig. 5, where curves for these two energy deposition pathways are compared at different incident neutron energies.

NIEL curves, i.e. non-ionizing energy depositions that produce further atom displacements, exhibit a steady rise with neutron energy up to about 0.1 MeV. At higher neutron energies the rise in NIEL is less pronounced, and once the energy gets to the MeV range a drop of NIEL is observed (see the 1 MeV curve in Fig. 3).

LET curves in Fig. 4, on the other hand, show that ionizing energy losses of Ti and O ions displaced by incident neutrons increase with neutron energy in the entire investigated range. The different dependences of ionizing and non-ionizing energy deposition pathways on neutron energy are observed even better from graphs in Fig. 5.

The shapes of NIEL and LET curves in Fig. 5 suggest another important issue. While at lower neutron energies both ionizing and non-ionizing energy losses occur primarily in the oxide region, at higher energies of incident neutrons high-energy PKAs and displaced ions lose energy primarily through ionizations, and as a result carry much of their energy away from the oxide and into platinum electrodes. Since the oxide, and particularly the stoichiometric TiO_2 layer, is particularly sensitive to non-ionizing energy deposition, i.e. to the formation of oxygen vacancies [4,8], it can be concluded that the memristor is more sensitive to irradiation by neutrons with energies below 0.1 MeV. It is above this energy that LET curves in Figs. 5 e)−g) are higher than NIEL curves and extend substantially beyond the oxide. At those same energies NIEL first reaches a maximum, and then drops at neutron energies in the MeV range.

The zero value of the horizontal depth axis in Figs. 2−5 is at the bottom of memristor structure, i.e. it starts at the bottom surface of the SiO_2 substrate. It is shown as the vertical axis on the right in Fig. 1.

IV. CONCLUSION

Coupled Monte Carlo simulation of neutron and secondary ion interactions in TiO_2 memristor structure was performed. Simulation results yielded the profiles of vacancy production, ionizing and non-ionizing energy deposition across the whole memristor stack, and most importantly in the oxide double-layer. Oxygen vacancies are produced uniformly across the whole oxide region at all investigated neutron energies (0.01−1 MeV). Non-ionizing energy loss is the prevalent energy deposition pathway at neutron energies up to about 0.1 MeV. At higher neutron energies, deposition of energy through ionizations by secondary displaced ions takes precedence. The oxide, and particularly the stoichiometric TiO_2 layer, is particularly sensitive to non-ionizing energy deposition, i.e. to the formation of oxygen vacancies. Since NIEL drops at neutron energies in the MeV range, and LET gets dispersed away from the oxide, electric properties of titanium dioxide memristors are expected to be affected most by neutrons with energies below about 0.1 MeV.

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