Supporting information:

**Synergistic Effect of Singly Charged Oxygen Vacancies and Ligand-Field for Regulating Transport Properties of Resistive Switching Memories**

D. Das†, A. Barman†, S. Kumar†, A. K. Sinha†,#, M. Gupta‡, R. Singhal§, P. Johari† and A. Kanjilal*  

*Corresponding author: aloke.kanjilal@snu.edu.in, priya.johari@snu.edu.in  
†Department of Physics, School of Natural Sciences, Shiv Nadar University, NH-91, Dadri, Gautam Buddha Nagar, Uttar Pradesh 201 314, India  
|Synchrotron Utilization Section, Raja Ramanna Center for Advanced Technology (RRCAT), Indore, Madhya Pradesh 452013, India  
# Homi Bhabha National Institute, Anishaktinagar, Mumbai-94, India  
‡UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore, Madhya Pradesh-452001, India  
§Department of physics, Malaviya National Institute of Technology Jaipur, JLN Marg, Malaviya Nagar,Jaipur-302017,India
S1. X-ray absorption near edge structure (XANES)

![XANES spectrum](image)

**Figure S1.** X-ray absorption near edge structure (XANES) spectra at the Ti-\(K\) edge, inset is showing the pre-edge feature.

XANES measurements were carried out in fluorescence mode at ambient pressure and room temperature at Indus-2, BL-12 RRCAT India. The details of the experimental setup and the beamline can be found elsewhere.\(^1\)\(^-\)\(^2\) At first, data of the standard anatase-\(\text{TiO}_2\) powder was recorded. Then, the position of the Ti-\(K\) edge was obtained from the standard XAS database of Hephaestus.\(^3\) Further, energy correction was performed for \(a\)-\(\text{TiO}_2\) samples to get the correct edge position. Finally, spectra were normalised to photon intensity and presented.
S2. Evolution of $\alpha$-TiO$_2$ (at various temperatures) structure through Molecular dynamics simulation

**Figure S2.** Evolution of $\alpha$-TiO$_2$ structure at various temperatures (a) starting structure ($R$-TiO$_2$) (b) 4800K (c) 2400K (d) 300K. Here blue and red atoms denote titanium and oxygen respectively.
S3. Average Ti-O bond length in $a$-TiO$_2$ and their distortion index

![Figure S3.](image)

**(a)** Average Ti-O bond length of 48 polyhedra in DFT simulated $a$-TiO$_2$ structure and **(b)** distortion in their bond length.

Here, distortion index ($DI$) in bond length is defined as,$^{4-5}$

$$ DI = \frac{1}{n} \sum_{i=1}^{n} \frac{|b_i - b_{av}|}{b_{av}} $$

(1)

where, $b_{av}$ is the average bond length of each polyhedron and $b_i$ is the distance of the $i$-th oxygen atom from the central Ti atom.
S4. Density of states of oxygen vacancies at different charge state

**Figure S4.** Projected density of states of different oxygen vacancies (a) $V_0^0$, (b) $V_0^{+1}$ and (c) $V_0^{+2}$. Here blue and brown coloured lines describe the contribution from Ti-$d$ and O-$p$ orbitals respectively.
S5. The details of the Monte-Carlo (MC) Simulations

We briefly describe below the Metropolis-Hastings algorithm based Monte Carlo simulation scheme,\textsuperscript{6-8} which has been employed in the present study to observe the formation of the conducting filaments.\textsuperscript{9-11}

a. The balance condition and acceptance probability

Suppose, we move from step $i$ to $i+1$ in the Markov chain then change in microstate probability $\varrho_m$ can be written as

$$\varrho_m(i+1) = \varrho_m(i) - \sum_n T_{mn} \varrho_m(i) + \sum_n T_{nm} \varrho_n(i) \quad (2)$$

Here $T_{mn}$ denotes the transition probability from state $m$ to $n$, similarly $T_{nm}$ for state $n$ to $m$. Since $\varrho_n(i+1) = \varrho_n(i)$ is always true for the Markov Process and also at equilibrium probability do not change with time, therefore

$$T_{mn} \varrho_m(i) = T_{nm} \varrho_n(i) \quad \text{for all } m, n \quad (3)$$

This is detailed balanced equation using it we can write the transition probability as the product of two terms.

$$T_{mn} = \alpha_{mn} p_{mn}^{acc} \quad (4)$$

$\alpha_{mn}$ is the random move proposal probability from state $m$ to $n$ and $p_{mn}^{acc}$ is the acceptance probability, now the using the detailed balance condition (3) we get:

$$\frac{p_{mn}^{acc}}{p_{nm}^{acc}} = \frac{\alpha_{nm} \varrho_n}{\alpha_{mn} \varrho_m} \quad (5)$$

For symmetric moves, the move proposal probabilities are equal in forward and reverse directions $\alpha_{mn} = \alpha_{nm}$, therefore,

$$\frac{p_{mn}^{acc}}{p_{nm}^{acc}} = \frac{\varrho_n}{\varrho_m} \quad (6)$$

We have $\varrho_m = e^{-\beta U_m}/Z$ and $\varrho_n = e^{-\beta U_n}/Z$ therefore we get
\[
\frac{P_{\text{acc}}^{mn}}{P_{\text{acc}}^{nm}} = \frac{e^{-\beta U_n} dr^N / Z}{e^{-\beta U_m} dr^N / Z} = e^{-\beta(U_n - U_m)} \tag{7}
\]

This is the acceptance criterion of the MC moves; we can choose the move as if it satisfy the above equation. In the Metropolis algorithm the acceptance criterion is given by

\[
P_{\text{acc}}^{mn} = \min\left[1, e^{-\beta(U_n - U_m)}\right] \tag{8}
\]

If, \(U_n < U_m\) then \(P_{\text{acc}}^{mn} = 1\) else, \(P_{\text{acc}}^{mn} = \frac{1}{e^{\beta(U_n - U_m)}}\)

b. The details of the Metropolis algorithm is given as follows

1) Consider a canonical ensemble with \(N\) number of particles, which are randomly distributed in a cubical box of length \(L\).

2) Determine an energy function \(U_m\) to describe the ensemble.

3) Pick up a particle \(i\) randomly from the distribution.

4) Apply \(\Delta r\) amount of perturbation on each of its \(x\), \(y\), and \(z\) coordinates of \(i\)-th particle.

5) Calculate the new energy function \(U_n\) to find the change in energy \(\Delta U = U_m - U_n\) caused due to the perturbation.

6) Use Metropolis algorithm to decide the acceptance of movement, if \(\Delta U < 0\) , accept the change and update the configuration, else in case of \(\Delta U < 0\), the configuration is accepted with a certain probability, the probability function defined as \(p_\alpha = e^{-\Delta U/kT}\). Generate a random number, \(\alpha \in [0,1]\), if \(\alpha < p_\alpha\) then the new configuration is accepted otherwise reject the move and update the configuration accordingly.

7) Repeat the process from step-3 onwards for all other particles to achieve the final configuration.
c. The optimised parameters used in MC simulation

<table>
<thead>
<tr>
<th>Simulation box size (L)</th>
<th>50nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$0.753 \times 10^{-3} \text{eV/Å}$</td>
</tr>
<tr>
<td>B</td>
<td>$11.83 \text{eV/Å}^2$</td>
</tr>
<tr>
<td>C</td>
<td>$383.45 \text{eV/Å}^6$</td>
</tr>
<tr>
<td>$U_0$</td>
<td>$10^8 \text{eV/cm}$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>$12^\circ$</td>
</tr>
<tr>
<td>Number of particles ($n$)</td>
<td>108</td>
</tr>
</tbody>
</table>
References


