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Supporting Information

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Biorealistic Implementation of Synaptic Functions with Oxide Memristors through Internal Ionic Dynamics

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Supplementary Information

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I. Device Fabrication

The memristor device consists of a MIM structure in a crossbar form with a palladium (Pd) top electrode, a tungsten oxide (WO_x) switching layer and a tungsten (W) bottom electrode, as schematically illustrated in **Figure S1**. First, 60 nm thick tungsten film was deposited by RF sputtering at room temperature on a thermally oxidized (200nm SiO_2) silicon substrate. The tungsten film was then patterned by e-beam lithography and reactive ion etching (RIE) to form the nanowire (300nm wide) bottom electrodes and the contact pads. Rapid thermal annealing (RTA) in pure oxygen at 375 ^oC for 1 minute was performed to form a tungsten oxide layer (~60nm) by partially oxidizing the W layer. Finally, the Pd/Au nanowire top electrodes was formed by e-beam lithography and lift-off processes, followed by tungsten oxide etching outside the cross-point regions using RIE to open the contact pads.

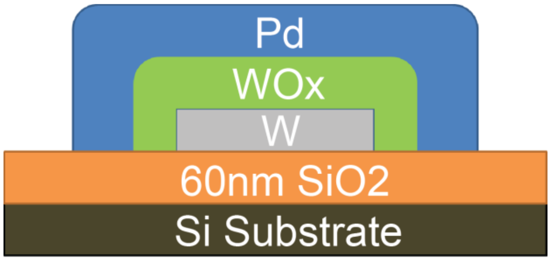

Figure S1. Schematic of the WO_x memristor structure

II. Electrical Characterization

The measurements were performed in a probe station (Model: TTP4, Desert Cryogenics, Lake Shore Cryotronics, Inc.) using a customized Matlab program to control a DAQ board (Model: USB-6259, National Instrument) to generate the desired voltage signals. The current was measured by a preamplifier (Model: 1211, DL Instrument, LLC) and collected by the DAQ board.

III. Oxygen Distribution in WO_x Memristor

Stoichiometry of tungsten oxide films depends on the fabrication process. It has been reported that longer oxidation of tungsten at temperatures of 300°C or higher yields larger W^{5+} to W^{6+} ratios.[1] This may be explained by the fact that the as-grown amorphous phase of tungsten oxide is changed to a (poly-) crystalline phase in which V_O segregate at the grain boundaries[1] under high temperature.

We performed X-ray diffraction (XRD) to analysis the crystallinity of the WO_x films prepared under different conditions.

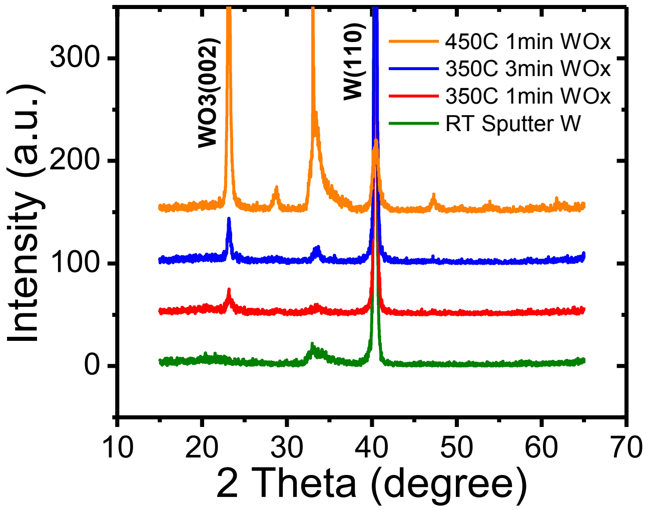

Figure S2. XRD patterns of W and RTA-oxidized WO_x films prepared at different oxidation temperatures and oxidation times.

Figure S2 shows the XRD spectra of the rapid-thermal-annealing (RTA)-oxidized WO_x films used in this study. It can be seen that WO_x films oxidized at 450 ^{0}C shows larger crystalline signals than that at 350 ^{0}C; also longer oxidation time (e.g. 3 min) leads to larger crystalline signals compared with shorter oxidation time (e.g. 1 min). Since the WO_x film grows from the WO_x/W interface, the portion near the top surface is grown first and will experience the longest oxidation/annealing time, leading to grain formation and more V_O accumulation near the top of WO_x layer at equilibrium.

A second factor is the possible oxygen diffusion through the top Pd electrode during the top Pd electrode evaporation process, as has been discussed by Joo et al,[2] which also generates V_O near the top surface.

IV. Memristor Device Model

In our modeling, we assume that the top Pd/WO_x interface is always Ohmic and behaves as an oxygen reservoir. When a positive voltage is applied on the top electrode, oxygen vacancies drift towards the bottom electrode, increasing the V_O concentration in localized channels and increasing the overall device conductance. The rest of the V_O deficient region remains in the low-conductance state and form a Schottky contact with the bottom W electrode.

As discussed in the main text, the memristor equations can be written as:

$$I = (1 - w_c) * \alpha * [1 - exp(-\beta V)] + w_c * \gamma * sinh(kV) \qquad \text{(S1)}$$

$$\frac{dw_m}{dt} = \lambda_m W(w_m, V)\, sinh(\rho_m |V|) - \frac{w_m - w_{m0}}{\tau_m^*(w_m)} \tag{S2}$$

$$\frac{dw_c}{dt} = \lambda_c\, W(w_c, V) exp(\epsilon w_m)\, sinh(\rho_c V) - \frac{w_c - w_{c0}}{\tau_c^*(w_m)} \tag{S3}$$

$$\frac{1}{\tau_m^*(w_m)} = \frac{w_m}{\tau_s} \tag{S4}$$

$$\frac{1}{\tau_c^*(w_m)} = \frac{1}{\tau_l} + \frac{\sigma \cdot w_m}{\tau_s} \tag{S5}$$

$$W(w, V) = \begin{cases} 1 - \exp\left(-\frac{w_{max} - w}{0.0001}\right) & if\ V \geq 0 \\ 1 - \exp\left(-\frac{w - w_{min}}{0.0001}\right) & if\ V < 0 \end{cases} \tag{S6}$$

Here Equation S1 is the current-voltage equation determined by the state variable w_c, which represents the effective area of the conducting region. Equation S2 and S3 are the dynamic equations of the two state variables w_m and w_c, in which the first term describes the effect of the stimulation voltage, while the 2nd term describes the effect of decay with different effective time constants ($\tau_m^*(w_m)$ and $\tau_c^*(w_m)$). The effectiveness of the stimulation on w_c is also affected by the mobility of the oxygen vacancies through the $exp(\epsilon w_m)$factor. The effective decay time constant $\tau_m^*(w_m)$ was chosen as in the form in Equation S4 to better capture the stretch-exponential type of decay instead of simple exponential decay. The effective decay time constant for w_c $\tau_c^*(w_m)$ is chosen in the form of Equation S5 so that when t is small (consequently when w_m is large), $\tau_c \sim \tau_s / \sigma w_m$ so the conductance decay follows the fast, short-time decay constant, while when t is large (consequently when w_m is small) $\tau_c \sim \tau_l$ and the conductance decay follows a much longer decay time constant. Equation S6 is window function $W(w,V)$ used in Equation S2 and S3 to account for the non-linear state-dependent programming effects.

The memristor model has been successfully implemented in a commercial simulation software LTSPICE. Significantly, the model based on these two state variables not only accurately captures the two-stage decay behavior shown in Figuare 1c, but also quantitatively explained all experimental behaviors including PPF, experience-dependent state change, sliding threshold effect and STDP, as shown in Figuare 2-5, using essentially a single set of material-dependent parameters.

Table S1 lists the parameters used in the simulation.

Parameter	Value	Parameter	Value
α	1.5e-6	β	4
γ	3.2e-6	κ	5
λ_m	1e-6	λ_c	1e-6
ρ_m	15.5±2.5	ρ_c	14±2
w_{c0}	0-0.3	W_{m0}	0.001
τ_s	0.0025	τ_l	298
σ	0.25	ϵ	15

Table S1. Memristor parameters used in simulation

In the simulation, all parameters were fixed except ρ_m and ρ_c, which are allowed to change slightly in different experiments to account for the small variations in the length of the V_O poor region in different devices and cycles, which affects the electric field applied to the V_Os to cause V_O migration. w_{c0} is the initial value before the simulation and its values are also listed in **Table**

S2. The initial value of w_{m0} is always fixed to be 0.001 (e.g. close to 0). The exact values of ρ_m , ρ_c and w_{c0} used in the simulations are listed in Table S2:

	ρ_m	ρ_c	w_{c0}
Fig. 2(c)	15.8	14.2	0
Fig. 2(d)	13	13	0.05
Fig. 3(b)	17	14.5	0.001
Fig. 3(c)	15	12.5	0.02
Fig. 3(d)	14.5	12	0.1
Fig. 4(a)	16.4	14.4	0.001
Fig. 5(b)	17.9	15.8	0.3

Table S2. Different values of ρ_m, ρ_c and w_{c0} used in several simulations

V. Explanation of STDP

Two key factors accounting for STDP: 1) the second pulse in a pulse pair determines the sign of the long-term weight change and 2) the effectiveness of the pulse pair is larger with shorter interval inside the pulse pair, can be explained by the residue w_m effect in the two-state-variable memristor model as shown in **Figure S3**.

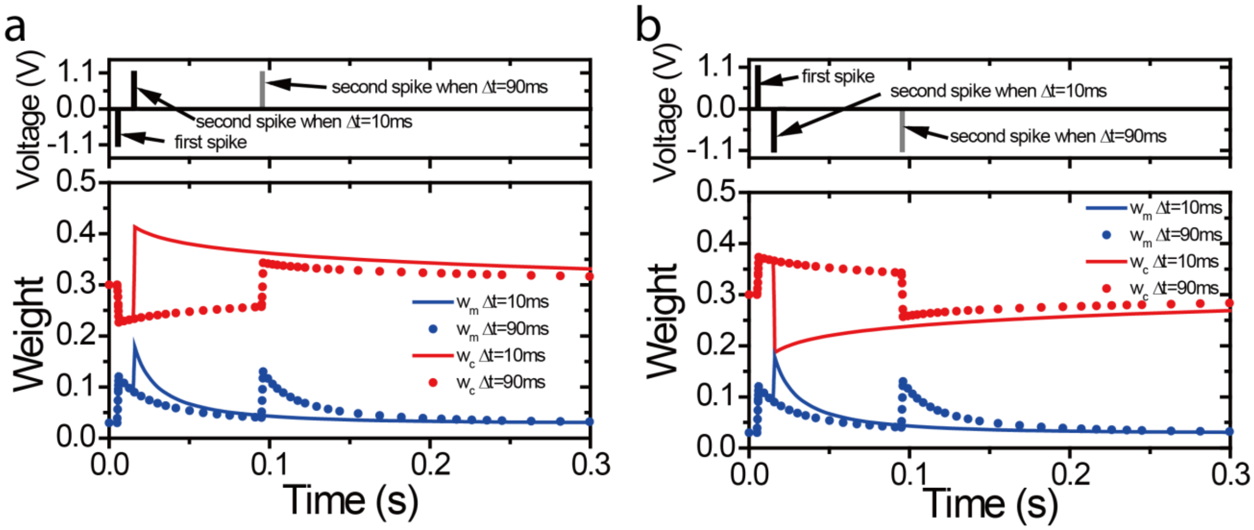

Figure S3. Simulation results illustrating how STDP is obtained with simple, non-overlapping pulses. Results of different intervals (Δt=10 ms and 90 ms) highlighting how w_m and w_m evolves are shown for both a) pre-post (potentiation) condition and b) post-pre (depression) condition. The effect of the 2nd pulse is enhanced due to the residue enhanced w_m (enhanced from the first pulse). As a result, a shorter interval leads to a larger w_m enhancement at the moment of the 2nd pulse and a larger potentiation or depression effect, depending on whether Δt is positive or negative.

VI. LTSPICE Code:

```
****************** LTspice code for metal oxide memristors*****************

*Parameters:

*alpha is prefactor for Schottky barrier

*beta is exponent for Schottky barrier

*gamma is prefactor for tunneling

*delta is exponent for tunneling
```

```
  ***********************************************************************************
.SUBCKT memristor 1 2 params:
+ alpha=1.5e-6 beta=4 gamma=3.2e-6 delta=5 wmax=1 wmin=0
*State variable:
.param lambda=1e-6 rhoc=14.5 rhom=17 taul=298 taus=0.0025 epsilon=15 sigma=0.25
.param cc={1}
.param cm={1}
Cpvar1 c 0 {cc}
Cpvar2 m 0 {cm}
*rate equation considering the diffusion effect
Gc 0 c value={trunc1(V(1,2),cc*V(c))*(lambda*exp(epsilon*cc*V(c))*sinh(rhoc*V(1,2)))-
(cc*V(c)-0.001)*(1/taul+sigma*cm*V(m)/taus)}
Gm 0 m value={trunc2(V(1,2),cm*V(m))*(lambda*sinh(rhom*abs(V(1,2))))-(cm*V(m)-
0.001)*(cm*V(m)/taus)}
.ic V(c) = 0.001
.ic V(m) = 0.001
****************************************************************
*auxiliary functions to limit the range of w
.func sign2(var) {(sgn(var)+1)/2}
.func trunc1(var1,var2) {sign2(var1)*sign2(wmax-var2)*(1-exp(-(wmax-var2)/0.0001))+sign2(-
var1)*sign2(var2-wmin)*(1-exp(-(var2-wmin)/0.0001))}
.func trunc2(var1,var2) {sign2(var1)*sign2(wmax-var2)*(1-exp(-(wmax-var2)/0.0001))+sign2(-
var1)*sign2(var2-wmin)*(1-exp(-(var2-wmin)/0.0001))}
```

```
***********************************************************************************

*Output:

Gw 1 2 value={(1-cc*V(c))*alpha*(1-exp(-beta*V(1,2)))+(cc*V(c))*gamma*sinh(delta*V(1,2))}

.ENDS memristor
```

References:

[1] C. Bittencourt, R. Landers, *Semicond. ...* **2002**, *522*.

[2] J.-H. Joo, J.-M. Seon, Y.-C. Jeon, K.-Y. Oh, J.-S. Roh, J.-J. Kim, *Appl. Phys. Lett.* **1997**, *70*, 3053.