Comprehensive numerical modeling of filamentary RRAM devices including voltage ramp-rate and cycle-to-cycle variations: Supplementary Material

Dipesh Niraula* and Victor Karpov†
Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606, USA

I. DEVICE MODEL

We modeled TiN/Hf/HfO_2/TiN multi-layered RRAM device having a cross-sectional area of 20nm × 20nm as reported in [1] and [2]. However, cylindrical geometry of 10 nm radius as in Fig. 1 was considered instead to reduce the 3D to 2D geometry by exploiting the rotational symmetry about the longitudinal axis of the cylindrical shape.

Fig. 1 (top) shows the device model used for ON and SET modules whereas Fig. 1 (bottom) for OFF and RESET modules. Although ON and SET modules utilizes same device model, the filament remains fixed throughout ON whereas it radially evolves in SET. Similarly, the gap remains fixed throughout OFF module whereas it longitudinally evolves in RESET module.

Following the algorithm below, one can simulate RRAM device in COMSOL.

A. COMSOL Algorithm

Following algorithm pertains to COMSOL version 5.3a.

1. Open **Model Wizard**
2. Select **2D Axisymmetric** as **Space Dimension**
3. Select **AC/DC module** and add **Electric Currents** and **Electrical Circuit** submodules
4. Select **Heat Transfer Module** and add **Heat Transfer in Solids** submodule
5. Select **Done**
6. Create **Geometry** of the device as in Fig. 1
7. Create **Blank Materials** in the **Materials** node and add material parameters from Table I
8. To add the experimental temperature-dependent electric conductivity,
   - from **Definitions** node, select **Functions** then **Interpolation**, and then insert temperature and corresponding conductivity values in the given table
   - select **Linear** in both **Interpolation** and **Extrapolation** option
9. To add the temperature and voltage dependent hopping conductivity,
   - from **Definitions** node, select **Variables**, add the formula from Table I, and then select the corresponding domain.
   - Note: the argument of the exponential and logarithm function must be unitless
10. Assign the materials to the corresponding domain.
11. In **Electric Currents** submodule,
    - add **Terminal** boundary condition, select the top boundary of the top electrode, and then

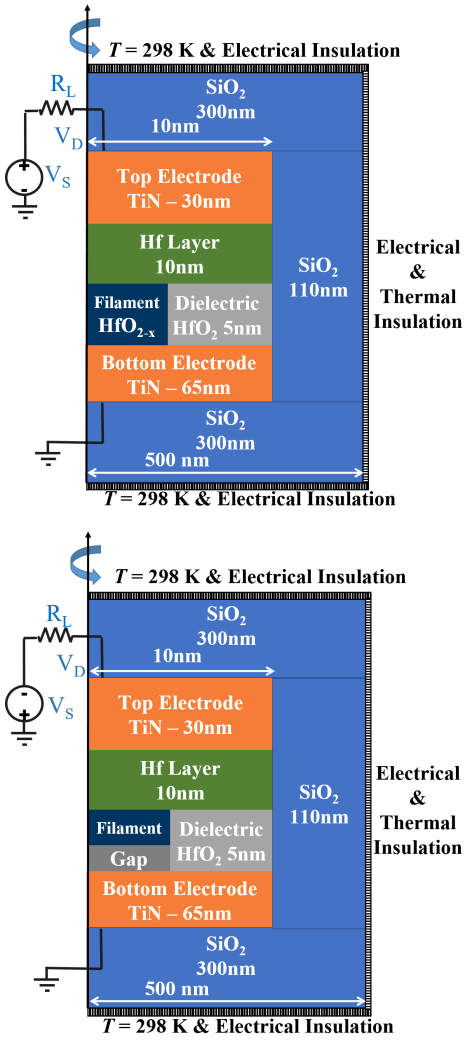

FIG. 1: Schematic of multi-layered RRAM cross-section. Top and bottom figures correspond to model used to emulate SET/ON and RESET/OFF process respectively. The figures include geometric parameters and material names of the devices various layers, and the boundary conditions. Note: Figure not drawn to scale.

*Electronic address: dipesh.niraula@rockets.utodeo.edu
†Electronic address: victor.karpov@utoledo.edu

TABLE I: Material parameters [3–5]

Material	σ_c[S/m]	κ[W/K.m]	C_p[J/kg.K]	ϵ_r [c]	ρ[kg/m^3]
SiO_2	10^{-9}	1.38	703	3.9	$2.2{\cdot}10^3$
TiN	Exp. $\sigma_c(T)$ [a]	$\sigma_c(T)TL$ [d]	545.33	-∞ [f]	$5.22{\cdot}10^3$
Hf	Exp. $\sigma_c(T)$ [b]	$\sigma_c(T)TL$ [d]	144	-∞ [f]	$13.3{\cdot}10^3$
HfO_2	10	0.5	120	25	$10{\cdot}10^3$
HfO_{2-x}	$\sigma_{0f}\exp\left(-\alpha_f \ln\left(\frac{\tau}{\tau_0}\right)\right)\exp\left(\sqrt{\frac{eV}{kT}}\right)$	$\sigma_c(T,V)TL$ [d]	140 [e]	-∞ [e,f]	$12{\cdot}10^3$ [e]
Gap	$\sigma_{0g}\exp\left(-\alpha_g \ln\left(\frac{\tau}{\tau_0}\right)\right)\exp\left(\sqrt{\frac{eV}{kT}}\right)$	$\kappa_{\text{eff}}\sigma_c(T,V)TL$ [d]	120 [g]	25 [g]	$10{\cdot}10^3$ [g]

[a] E. Langereis et al., *J. Appl. Phys.* **100**, 023534 (2006).
[b] P.D. Desal, et al., *J. Phys. Chem. Ref. Data.* **3**, 1069 (1984).
[c] Relative Permittivity
[d] Wiedemann–Franz–Lorenz law
[e] Assumed value such that it lies in between Hf and HfO_2
[f] -10^6 was used instead of -∞ for practical purpose
[g] Assumed to be equal to that of HfO_2

TABLE II: Various parameters

Parameters	Value
Circuitry[1]	
R_L	3.1 kΩ
$V_{\text{amp(+ve)}}$, $V_{\text{amp(-ve)}}$	1.25 V, -1.75 V
λ	100 V/s, 10 kV/s, 1 MV/s
Electric Conductivity (gap/filament)	
σ_{0f}	5 kS/m
σ_{0g}	3 kS/m
α_f	-0.05
α_g	0.05
τ	V_{amp}/λ
$\tau_0(\tau_{\min})$	0.1 ps
Thermal Conductivity (gap)	
κ_{eff}	10
Chemical Energy[7]	
σ	0.01 J/m^2
$\overline{\delta\mu_1}$	10 GJ/m^3
$\overline{\delta\mu_2}$	6.5 GJ/m^3
β_1	0.35 GJ/m^3
β_2	0.5 GJ/m^3
ΔW_{Buc}	1.0 eV
ΔW_{Bi}	0.1 eV
ΔW_{Bmc}	0.3 eV
Filament Nucleation[6]	
h	5 nm
W_0	2.5 eV
Λ	6.6
r_c	2.9 nm
$r_{\min}$	0.5 nm
α	$r_{\min}/r_c$
Static Disorder	
α_f	rand(-0.07, -0.03) [h]
α_g	rand(0.03, 0.07) [h]
σ_{0f}	rand(2,8) kS/m [h]
σ_{0g}	rand(1,5) kS/m [h]
$\overline{\delta\mu_1}$	rand(8.5,11.5) GJ/m^3 [h]
$\overline{\delta\mu_2}$	rand(5.5, 7.5) GJ/m^3 [h]
W_0	rand(2.4, 2.6) eV [h]

[h] function rand(x,y) produces uniformly distributed random number between x and y

select **Circuit** as the **Terminal type**
- add **Ground** boundary condition and select the bottom boundary of the bottom electrode
- Note: **Electric Currents** submodule has four necessary default subnodes

12. In **Electric Circuit** submodule,
    - add **Resistor** and insert the value of load resistance,
    - add **External I Vs. U** from **External Coupling** and select **Terminal voltage** from **Electric potential** option
    - add **Voltage Source** for OFF, ON, and RESET modules and **Current Source** for SET module
    - select **DC-Source** as **Source type** for SET and RESET modules then insert the source current or voltage value
    - select **Pulse source** as **Source type** for ON and OFF modules and define the pulse length according to the different ramp-rate as listed in Table. II
    - Note: every component has positive **p** and negative **n** node names under **Node Connections** which enables to position a component in the circuit. For example, **Ground Node** is **0** by default; to ground the voltage source, insert **0** in the **n** node name
    - Note: **Electric Circuit** submodule has one necessary default subnode
13. In **Heat Transfer in Solids** submodule,
    - add **Temperature** boundary condition, select the top boundary of the SiO_2 superstrate and bottom boundary of the SiO_2 substrate, and choose 298K in the user defined temperature section.
    - add **Diffusive Surface** boundary condition, select all the inner boundaries, and then choose 298K in the user defined temperature section and 0.9 in the user defined **Surface emissivity** section
    - Note: **Heat Transfer in Solids** submodule has four necessary default subnodes

14. In **Multiphysics** node, to couple the **Electric Currents** and **Heat Transfer in Solids** submodule,
    - select all the domains and boundaries in **Electromagnetic Heating** sub-node
    - select **Heat Transfer in Solid** as **Source** and **Electric Currents** as **Destination** in **Temperature** sub-node
15. Create **Mesh**
    - either automatic **Physics-controlled mesh** or manual **User-controlled mesh** can be selected
    - **Free Triangular** meshes of different sizes were manually defined for our simulation–to define the mesh size, add **Size** in **Free Triangular** mesh, then use either the **Predefined** or the **Custom** option
    - select **Build All**
16. Select **Study** type
    - select **Time Dependent** study for ON and OFF modules and then add **Times** corresponding to the pulse lengths
    - select **Stationary** study for SET and RESET modules
17. Select **Compute**
18. Obtain results in desired form from the **Results** node

B. Differential Equations

For ON and OFF modules, COMSOL solves the following time-dependent equations,

1. **Electric Currents** module:

$$\boldsymbol{\nabla}.\boldsymbol{J} = 0, \quad \boldsymbol{J} = \sigma_c \boldsymbol{E} + \epsilon \frac{\partial \boldsymbol{E}}{\partial t}, \quad \boldsymbol{E} = -\nabla V. \tag{1}$$

2. **Heat Transfer in Solids** module:

$$\rho C_p \frac{\partial T}{\partial t} - \nabla.(\kappa \nabla T) = Q_s. \tag{2}$$

3. **Multiphysics** module:

$$Q_s = \boldsymbol{J}.\boldsymbol{E}. \tag{3}$$

For SET and RESET module, COMSOL solves the following stationary equations,

1. **Electric Currents** module:

$$\boldsymbol{\nabla}.\boldsymbol{J} = 0, \quad \boldsymbol{J} = \sigma_c \boldsymbol{E}, \quad \boldsymbol{E} = -\nabla V. \tag{4}$$

2. **Heat Transfer in Solids** module:

$$-\nabla.(\kappa \nabla T) = Q_s. \tag{5}$$

3. **Multiphysics** module:

$$Q_s = \boldsymbol{J}.\boldsymbol{E}. \tag{6}$$

In the above equations, $\boldsymbol{J}$ is the current density, σ_c is the electric conductivity, $\boldsymbol{E}$ is the electric field, κ is the thermal conductivity, and Q_s is the heat source. Equations in Eq. (1) and (4) are the current conservation law, Ohms law, and the relation between electric field and electric potential due to Maxwell law respectively. Equations (2) and (5) are the Fourier heat law where the heat source is represented by the Joule heat terms in Eqs. (3) and (6). The Multiphysics module couples the Electric Currents and Heat Transfer in Solids modules to define the electromagnetic heat source.

C. Boundary Conditions

The required boundary conditions are listed below.

1. **Electric Insulation** ($\boldsymbol{n}.\boldsymbol{J} = 0$)
   All three boundaries of the SiO_2 domain are electrically insulated. Here **n** is the unit vector normal to the surface boundary.
2. **Ground** ($V = 0$)
   Interface common to the bottom electrode and SiO_2 substrate is grounded.
3. **Terminal** ($V = V_D$ or $I = I_S$)
   Interface common to the top electrode and SiO_2 superstrate is connected to the power-source and load resistor in series. **Terminal** handles both voltage source and current source.
4. **Temperature** ($T = 298$ K)
   Free surfaces of both SiO_2 layers are placed at room temperature, assuming they are in contact with a larger body which acts as a heat sink and maintains room temperature. Also, all three boundaries of the SiO_2 domain are at room temperature.
5. **Diffuse Surface** ($-\boldsymbol{n}.\boldsymbol{q} = \sigma_B(T_{\text{amb}}^4 - T^4)$)
   All the interface of the device loses heat through radiation governed by Stefan-Boltzmann law. Here q is the power radiated per surface area, σ_B is the Stefan-Boltzmann constant, and T_{amb} is the ambient temperature (298 K).

D. Parameters

The geometric parameters are presented in Fig. 1 and coefficients of the differential and free energy equations used for the modeling are listed in Table. I and II. We have verified that our modeling results are not critically sensitive to either of those parameters. In particular, these parameters change from cycle to cycle. Therefore, the degree of sensitivity of our results to the model parameters can be assessed from the cycle-to-cycle variations in IV curves presented in the last figure of the main text.

II. MINIMIZATION ALGORITHM

This section presents two sets of the minimization algorithms corresponding to SET and RESET process, formulated for a computer program followed by the details of the method applied.

A. SET Process

1. construct a device
2. fix the current and calculate free energy of the device for all filament radii: 0 to device radius
3. find the minimum in the free energy with respect to filament radius ($\partial F/\partial r$) for a fix current
4. redo step 2 and 3 for all current values taking discrete steps
5. record the device I-V corresponding to the free energy minimum for all current
6. vertical SET I-V is obtained in step 5

B. RESET Process

1. construct a device
2. fix the source voltage and calculate free energy of the device for all gap width: 0 to insulator thickness
3. find the minimum in the free energy with respect to gap width ($\partial F/\partial l$) for a fix source voltage
4. redo step 2 and 3 for all source voltages taking discrete steps
5. record the device I-V corresponding to the free energy minimum for all source voltages
6. horizontal RESET I-V is obtained in step 5

C. Minimization Procedure

Brent's Method [8] is utilized to find the free energy minimum. The method details are not included in this report and can be found in any relevant standard text. However, one important detail is that the method will yield one of the boundary free energy values if there exist no minima in the range of filament radii/gap width. Thus, the minimization process is divided into two steps: (1) minimum in free energy is located with low resolution, (2) if there exist a minimum, then Brent's method is applied.

For instance, the free energy minimization with respect to filament radius was carried out ranging from 1 nm to device radius with a step (Δr) of 2 nm, then the minimum is searched, by applying the condition

$$\text{Is} \quad F(r_i + \Delta r) - F(r_i) > 0 \quad \text{and} \quad F(r_i) - F(r_i - \Delta r) < 0?$$

The value of r_i that yields true for the above condition is the stable radius (r_c), and $F(r_c)$ is the minimum for that resolution. If the condition is not satisfied by any filament radius, then there exists no minima for that particular current, and the program moves to next value of current. When the condition is satisfied, the program applies Brent's method for the filament range, $r_c - \Delta r$ to $r_c + \Delta r$. This yields a more accurate stable radius.

[1] A. Fantini, D.J. Wouters, R. Degraeve, L.Goux, L. Pantisano, G. Kar, Y.-Y. Chen, B. Govoreanu, J.A. Kittl, L. Altimime, and M. Jurczak, Intrinsic Switching Behavior in HfO2 RRAM by Fast Electrical Measurements on Novel 2R Test Structures, *2012 4th IEEE International Memory Workshop*, Milan, pp. 1-4 (2012).

[2] A. Fantini, L. Goux, R. Degraeve, D.J. Wouters, N. Raghavan, G. Kar, A. Belmonte, Y.-Y. Chen, B. Govoreanu, and M. Jurczak, Intrinsic switching variability in HfO_2 RRAM, *2013 5th IEEE International Memory Workshop, Monterey*, CA, pp. 30-33 (2013).

[3] Carl L. Yaws. *The Yaws Handbook of Physical Properties for Hydrocarbons and Chemicals*, 2nd ed. Gulf Professional Publishing, Houston, TX (2015).

[4] M. A. Panzer, M. Shandalov, J. A. Rowlette, Y. Oshima, Y. W. Chen, P. C. McIntyre, and K. E. Goodson, Thermal Propoerties of Ultrathin Hafnium Oxide Gate Dielectric Films, *IEEE El. Dev. Lett.*, **30**, 1269 (2009).

[5] B. Govoreanu, S. Clima, I. P. Radu, Y. Chen, D. J. Wouters, and M. Jurczak, Complementary Role of Field and Temperature in Triggering ON/OFF Switching Mechanisms in Hf/HfO_2 Resistive RAM Cells, *IEEE Trans. On El. Dev.*, **60**, 2471 (2013).

[6] V. G. Karpov, Y.A. Kryukov, I.V. Karpov, and M. Mitra, Field induced nucleation in phase change memory, *Phys. Rev. B*, **78**, 052201 (2008).

[7] V. G. Karpov, D. Niraula, I.V. Karpov, and R. Kotlyar, Thermodynamics of phase transitions and bipolar filamentary switching in resistive random-access memory, *Phys. Rev. Appl.*, **8**, 024028 (2017).

[8] W. H. Press, S. A. Teukolsky, W. T. Vetterling, B. P. Flannery, *Numerical Recipes in Fortran 77: the Art of Scientific Computing. Second Edition*, vol. 1, 1996.