

Development of an electro-thermal resistive switching model based on O-Frenkel pairs to study reset and set mechanisms in HfO₂-based RRAM cells

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Abstract—An electro-thermal resistive switching model based on O-Frenkel pairs is presented. This model relies on partial differential equations and is used to simulate reset and set mechanisms for HfO₂-based RRAM devices starting from an existing conductive filament. First simulations indicate that the model can fairly reproduce experimental ON and OFF resistances.

Keywords—oxide based RRAM simulation; switching model; O-Frenkel pairs;

I. INTRODUCTION

Oxide based RRAM memories are considered as potential candidates to replace floating gate memory devices due to their low power operation, high switching speed and compatibility with conventional CMOS back-end-of-line process. The formation and rupture of a conductive filament is generally known to be the mechanism that underlies resistive from a Low Resistive State (LRS) to a high resistive state (HRS). An electro-thermal resistive switching model based on O-Frenkel pairs is presented. This model relies on partial differential equations and is used to simulate reset and set mechanisms for HfO₂-based RRAM devices starting from an existing conductive filament. Simulated devices are 1T/1R HfO₂-based RRAM cells relying on 65nm CMOS technology. The cells stack consists of a 5nm thick HfO₂ layer sandwiched between bottom TiN(35nm) and top Ti(10nm)/TiN(50nm) electrodes. The resolution of the PDE system is coupled to an analytical model of a MOSFET transistor in order to simulate real devices under test.

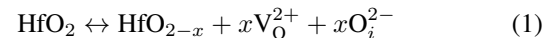
II. A SWITCHING MODEL BASED ON O-FRENKEL PAIRS

A. A filamentary conduction mechanism

Our model relies on a filamentary conduction mechanism based on the breaking of Hf-O bonds and migration of oxygen ions under high electric fields and elevated temperature. Starting from an existing partial derivative equations (PDE) model [1] based on a single type default migration model, we propose to go further by taking into account both oxygen interstitial ions and oxygen vacancies in order to be closer to switching physical mechanisms.

B. Switching model based on O-Frenkel pairs

Doubly charged oxygen vacancies V_O^{2+} and oxygen interstitials ions O_i^{2-} appear to be the most energetically favourable point defects that can be created in monoclinic HfO₂, as shown by *ab initio* calculations [2] [3] [4]. A possible physical interpretation of the switching mechanism is thus based on the creation of such defects as described by the following reaction:



III. PARTIAL DERIVATIVE EQUATIONS ELECTRO-THERMAL MODEL

A. Electric field driven ions migration model

Local temperature and electrostatic potential are derived from the self-consistent solution of current continuity equation (2) and heat equation (3) coupled to conservation equations for ions and vacancies:

$$\nabla \cdot (-\sigma \nabla V) = 0 \quad (2)$$

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k_{th} \nabla T) = \sigma (\nabla T)^2 \quad (3)$$

$$\frac{\partial n_{O_i^{2-}}}{\partial t} + \nabla \cdot (-D_{O_i^{2-}} (\nabla n_{O_i^{2-}}) + \nu_{O_i^{2-}} n_{O_i^{2-}}) = G - R \quad (4)$$

$$\frac{\partial n_{V_O^{2+}}}{\partial t} + \nabla \cdot (-D_{V_O^{2+}} (\nabla n_{V_O^{2+}}) + \nu_{V_O^{2+}} n_{V_O^{2+}}) = G - R \quad (5)$$

$$G = G_0 \exp\left(-\frac{E_{AG} - bE}{k_B T}\right) \quad (6)$$

$$R = 4\pi a_0 (D_{O_i^{2-}} + D_{V_O^{2+}}) \exp\left(-\frac{E_{AR}}{k_B T}\right) (n_{O_i^{2-}} n_{V_O^{2+}}) \quad (7)$$

Activation energies for oxygen ions and oxygen vacancies diffusion obtained from *ab initio* simulations indicate that

oxygen ions are much more mobile than oxygen vacancies [5] and this is included in our model (Tab.I). The source term G - R represents a net generation rate. The reset process is a dielectric local re-oxidation by the recombination of O-Frenkel pairs; the term R modelled according to Waite theory [6] is predominant during reset process. The set process is as a dielectric soft breakdown under stress voltage; the term G is predominant during set process and models the creation of O-Frenkel pairs under the action of the electric field. An expression proposed in [7] [8] is used and inspired by the McPherson model [9]. Parameters G_0 and E_{AG} which depend on intrinsic material properties are taken as fitting parameters. Diffusion and drift coefficients for V_{O}^{2+} and O_i^{2-} are modelled according to Mott-Gurney model [10] by:

$$D_{V_{O}^{2+}} = a^2 f \exp\left(-\frac{E_{A,V}}{k_B T}\right) \quad (8)$$

$$\nu_{V_{O}^{2+}} = 2af \exp\left(-\frac{E_{A,V}}{k_B T}\right) \sinh\left(\frac{zaE}{2k_B T}\right) \quad (9)$$

$$D_{O_i^{2-}} = a^2 f \exp\left(-\frac{E_{A,O}}{k_B T}\right) \quad (10)$$

$$\nu_{O_i^{2-}} = 2af \exp\left(-\frac{E_{A,O}}{k_B T}\right) \sinh\left(\frac{zaE}{2k_B T}\right) \quad (11)$$

TABLE I. PARAMETERS FOR FRENKEL-PAIRS MODEL

z	f	a	$E_{A,V}$	$E_{A,O}$	E_{AR}	E_{AG}	b
2e	10^{13} Hz	5Å	1.5eV	0.7eV	0.15eV	0.4eV	90eÅ

B. Local models of electrical and thermal conductivities

We consider that the accumulation of oxygen vacancies produces the conductive sub-oxide [1] [4]. In monoclinic HfO_2 , oxygen atom density is about $6 \cdot 10^{28}$ atom/m³; if the sub-oxide results from the transition HfO_2 to Hf_2O_3 , as studied in [4], oxygen concentration in the sub-oxide corresponds to an oxygen loss of 25%. Thus, oxygen vacancy concentration in the initial filament ($n_{D,max}$) is fixed to $1.5 \cdot 10^{28}$ atom/m³. Therefore, in current continuity equation (2) a local conductivity that depends on the local vacancy concentration is used for the oxide as proposed by [1]:

$$\sigma(n_{V_{O}^{2+}}) = \sigma_m \exp\left(-\frac{E_{AC}}{k_B T}\right) \quad (12)$$

where both σ_m and E_{AC} depend on the local vacancy concentration:

$$\sigma_m(n_{V_{O}^{2+}}) = \sigma_0 + \frac{\sigma_{max} - \sigma_{th}}{n_{D,max} - n_{th}} n_{V_{O}^{2+}} \quad (13)$$

$$E_{AC}(n_{V_{O}^{2+}}) = \begin{cases} E_{A0} - E_{A0} \frac{n_{V_{O}^{2+}}}{n_{th}} & \text{if } n_{V_{O}^{2+}} \leq n_{th} \\ 0 & \text{if } n_{V_{O}^{2+}} > n_{th} \end{cases} \quad (14)$$

TABLE II. PARAMETERS FOR OXIDE ELECTRICAL CONDUCTIVITY MODEL

$n_{D,max}$	n_{th}	E_{A0}
$1.5 \cdot 10^{28} \text{ m}^{-3}$	$1.5 \cdot 10^{27} \text{ m}^{-3}$	0.05eV
σ_{max}	σ_{th}	σ_0
$3 \cdot 10^5 \text{ S/m}$	$5 \cdot 10^4 \text{ S/m}$	10S/m

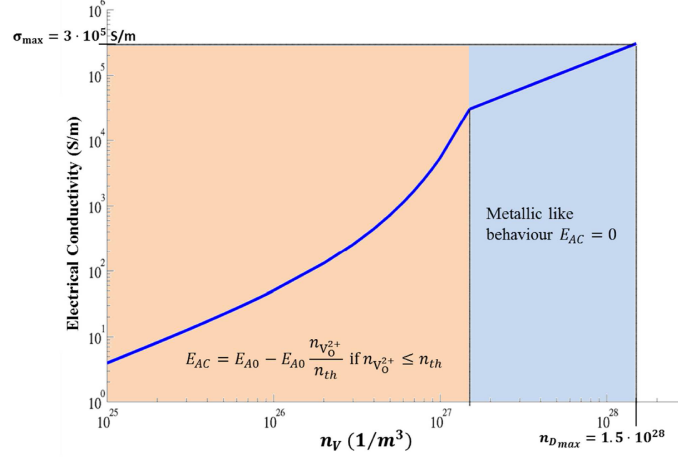


Fig. 1. Calculated electrical conductivity function of $n_{V_{O}^{2+}}$

Equation (14) is used to model the electrical behaviour: oxide conductivity locally tends to metal-like conductivity for an oxygen vacancy concentration higher than a threshold vacancy concentration (n_{th}) as illustrated by Fig.1. In this work, a filament with a 2nm radius is considered. Assuming this size for the filament, the parameters σ_{max} , n_{th} and σ_{th} (given in Tab.II) are fixed to get the simulated resistances close to the measured resistances at both the LRS and the HRS state. Regarding the thermal conductivity, we assume a linear dependence of k_{th} on the V_{O}^{2+} concentration as proposed in [1]:

$$k_{th} = k_s n_{V_{O}^{2+}} + k_0 \quad (15)$$

The values of the parameters given in Tab.III are fixed to get a thermal conductivity varying from 23W/m/K (Hf thermal conductivity) to 0.5W/m/K (HfO_2 thermal conductivity).

TABLE III. PARAMETERS FOR OXIDE THERMAL CONDUCTIVITY MODEL

k_s	k_0
$1.875 \cdot 10^{-27} \text{ Wm}^2/\text{K}$	0.5W/m/K

IV. TRAPPING MODEL OF OXYGEN IONS BY THE TITANIUM LAYER

The cells stack studied consists of a 5nm thick HfO_2 layer sandwiched between TiN(35nm) and Ti(10nm)/TiN(50nm) electrodes. Physical and chemical measurements have revealed that Ti induces the formation of a TiO_x/HfO_2 interfacial layer leaving the Hf oxide enriched of O-vacancies [2]. Moreover Ti is found responsible for activating bipolar switching. In this work we do neither simulate the forming step nor the growth of a TiO_x layer that takes place during the forming step. We introduce a simple model of trapping-release of oxygen ions by

the Ti layer. We consider that the result of the forming step is a significant O_i^{2-} concentration inside the Ti layer. Furthermore we model the transfer of O_i^{2-} between the Ti layer and the HfO_2 layer by a flux term at the Ti/ HfO_2 interface:

$$\Phi = h(n_{O_i^{2-}}(Ti) - n_{O_i^{2-}}(HfO_2)) \quad (16)$$

where h , the transfer coefficient, is modelled by:

$$h = \mu_0 E_n \exp\left(-\frac{E_{trap}}{k_B T}\right) \quad (17)$$

The transfer coefficient h is thermally activated to take into account the energy needed to break the Ti-O bound in the TiO_x layer and liberate the oxygen ions. Moreover its sign depends on the sign of E_n , the normal electric field at the Ti/ HfO_2 interface to inverse the flux when the applied polarity is inverted. Parameters μ_0 and E_{trap} are fitting parameters.

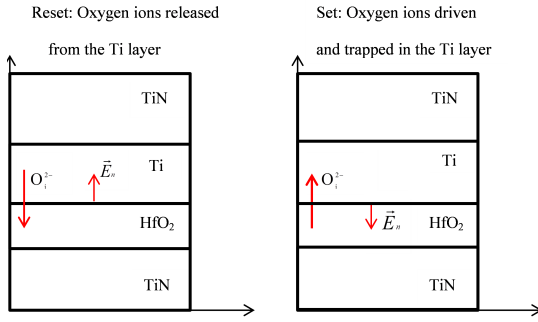


Fig. 2. Release and trapping of oxygen ions by the Ti layer

We consider that, during the forming step, oxygen ions are driven outside the HfO_2 layer by the electric field and accumulate in the Ti layer near the Ti/ HfO_2 interface. So we use a schematic Gaussian concentration of oxygen ions in the Ti layer as an initial condition for reset simulation. During reset operation, which corresponds to dielectric re-oxidation, oxygen ions are released from the Ti layer to the HfO_2 layer. During the set operation oxygen ions are driven outside the HfO_2 layer by the electric field and accumulate in the Ti layer near the Ti/ HfO_2 interface (a very small diffusion coefficient for oxygen ions in the Ti layer is used).

V. COUPLING WITH AN ANALYTICAL MODEL OF MOSFET TRANSISTOR

The model is implemented in the numerical toolbox COMSOL based on the Finite Element Method. The Partial Derivatives Equations system modelling the OXRAM is coupled to a circuit model including a voltage source and a transistor MOSFET to simulate the device under test (Fig.3).

The Electrical Circuit Interface found under the ACDC branch of COMSOL is used and the MOSFET model is calibrated from experimental data. In LRS state, the current is limited by the saturation current delivered by the transistor. Time-dependent electrical characteristics are simulated using a rectangular voltage pulse (V_{pulse}) delivering 1.5V during 10 μ s. The following electrical biases are applied to the device:

- for reset: $V_s = V_{pulse}(t)$, $V_g = 3V$, $V_a = 0V$
- for set: $V_s = 0V$, $V_g = 1.5V$, $V_a = V_{pulse}(t)$

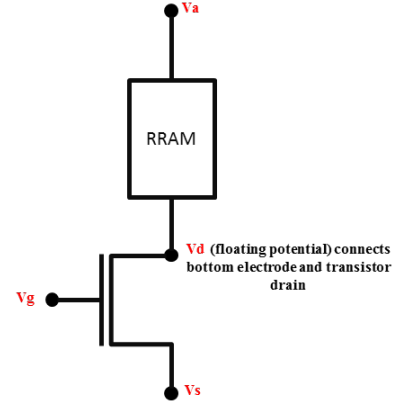


Fig. 3. Schematic of the device simulated

VI. SIMULATION RESULTS

Reset simulation starts from schematic concentrations of V_O^{2+} and O_i^{2-} as obtained after a forming step (Fig.6a). Axis symmetric representation is used. As indicated in (Fig.5), when the square pulse for the reset transition is applied to the device, the response current increases following the voltage increment because the state of the memory is the LRS state. In this state, the maximal current is around 400mA. Over time, the response current rapidly decreases, which indicates the moment of the reset transition. Simulated time for the reset pulse previously described is around 4 μ s for the reset pulse previously described. Recombination front corresponding to the re-oxidation of filament is illustrated by (Fig.7). The initial resistance obtained by our model for a schematic filament of radius 2nm is 48110 Ω . Low field resistance R_{off} (after reset simulation) is 48110 Ω . Set simulation (Fig.8) starts from concentrations of V_O^{2+} and O_i^{2-} obtained at the end of the reset pulse (Fig.6c). Low field R_{on} (after set simulation) is 4149 Ω . R_{off} and R_{on} are of the right order of magnitude when compared to experimental data (Fig.4) [11].

Calibration and numerical robustness of the set operation simulation will be improved; nevertheless the present simulation already leads to a partial reconstruction of the filament as shown by the vacancy concentration at the end of the set simulation (Fig.8).

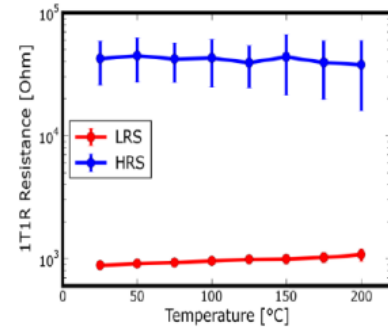


Fig. 4. Experimental resistances LRS and HRS

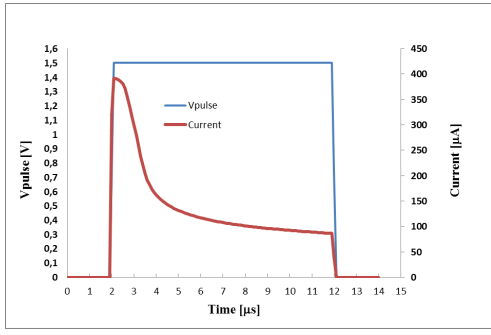


Fig. 5. Simulated current and V_{pulse} during reset

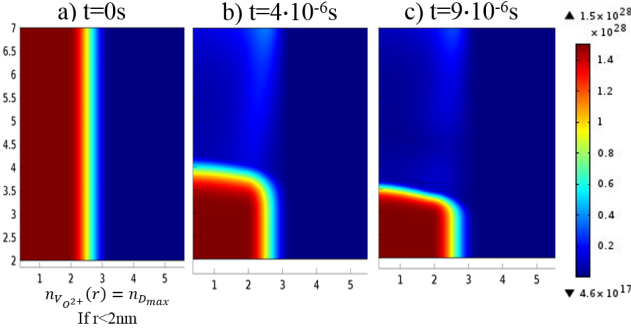


Fig. 6. Evolution of $n_{V_{O^{2+}}}$ during reset simulation

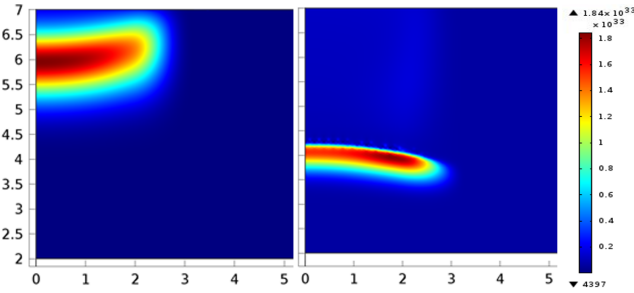


Fig. 7. Recombination term at $3\mu s$ end $4\mu s$ during reset

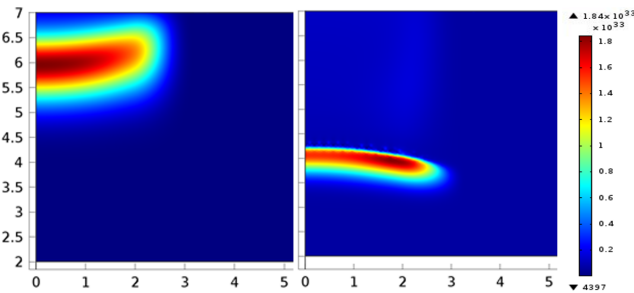


Fig. 8. $n_{V_{O^{2+}}}$ at $t=0s$ and $t=9\mu s$ during set simulation

VII. CONCLUSION

We have developed, in the toolbox COMSOL, a Finite-Element electro-thermal resistive switching model based on O-Frenkel pairs to study reset and set mechanisms in HfO_2 -based RRAM cells. The originality of this work lies in the simulation of both doubly charged oxygen vacancies $V_{O^{2+}}$ and oxygen

interstitials ions O_i^{2-} and in the modelling of trapping-release of oxygen ions by the Ti layer. Maximal oxygen concentration ($n_{D_{max}}$) has been fixed using oxygen atomic concentrations estimated from *ab initio* simulations; other parameters of the electrical model (σ_{max} , n_{th} and σ_{th}) have been chosen in order that simulated HRS and LRS (when we assume the forming steps produce an initial filament of 2nm radius) show good consistency with the experimental data. This model takes into account Frenkel pair generation and recombination, conservation equation for both oxygen vacancy and interstitial ions and the calculation of electrical characteristics of the device during reset and set operations. Therefore, it can be used to study the influence of some physical mechanisms at the atomic scale on the electrical characteristics of the cell. For example, different mechanisms for oxygen ions diffusion with distinct activation energies could be studied. Segregation of impurities at the Ti/ HfO_2 interface and its influence on the trapping of oxygen ions by the Ti layer could be included in this model. The validation of our model will be continued and its numerical robustness will be improved. The coupling of the reset-set model with a forming model should be considered.

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