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 cells relying on 65nm CMOS technology. The cell 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 V2+ and oxygen interstitials ions O2− 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:

\[ \text{HfO}_2 \leftrightarrow \text{HfO}_{2-x} + x\text{V}^{2+} + x\text{O}^{2-} \]  

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:

\[ \nabla \cdot (-\sigma \nabla V) = 0 \]  

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

\[ \frac{\partial n_{O^{2-}}}{\partial t} + \nabla \cdot (-D_{O^{2-}} \nabla n_{O^{2-}} + \nu_{O^{2-}/O} n_{O^{2-}} - n_{O^{2-}}) = G - R \]  

\[ \frac{\partial n_{V^{2+}}}{\partial t} + \nabla \cdot (-D_{V^{2+}} \nabla n_{V^{2+}} + \nu_{V^{2+}/V} n_{V^{2+}} + n_{V^{2+}}) = G - R \]  

\[ G = G_0 \exp \left(-\frac{E_{AG} - bE}{k_B T}\right) \]  

\[ R = 4\pi a_0 (D_{O^{2-}} + D_{V^{2+}}) \exp \left(-\frac{E_{AR}}{k_B T}\right) (n_{O^{2-}} - n_{V^{2+}}) \]
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 $O_2^-$ are modelled according to Mott-Gurney model [10] by:

$$D_{O_2^+} = a f \exp\left( -\frac{E_{A,V}}{k_B T} \right)$$  \hspace{1cm} (8)

$$\nu_{O_2^+} = 2af \exp\left( -\frac{E_{A,V}}{k_B T} \right) \sinh\left( \frac{za E}{2k_B T} \right)$$  \hspace{1cm} (9)

$$D_{O_2^-} = a f \exp\left( -\frac{E_{A,O}}{k_B T} \right)$$  \hspace{1cm} (10)

$$\nu_{O_2^-} = 2af \exp\left( -\frac{E_{A,O}}{k_B T} \right) \sinh\left( \frac{za E}{2k_B T} \right)$$  \hspace{1cm} (11)

### 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 $6 \cdot 10^{23}$atom/m$^3$; if the sub-oxide results from the transition HfO$_2$ to HfO$_3$, 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/m$^3$. 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]:

$$\sigma(n_{v_{O}^{2+}}) = \sigma_m \exp\left( -\frac{E_{AC}}{k_BT} \right)$$  \hspace{1cm} (12)

where both $\sigma_m$ and $E_{AC}$ depend on the local vacancy concentration:

$$\sigma_m(n_{v_{O}^{2+}}) = \sigma_0 + \frac{\sigma_{max} - \sigma_{th}}{n_{D_{max}} - n_{th}} n_{v_{O}^{2+}}$$  \hspace{1cm} (13)

$$E_{AC}(n_{v_{O}^{2+}}) = \begin{cases} E_{A0} - E_{A0} \frac{n_{v_{O}^{2+}}}{n_{th}} & \text{if } n_{v_{O}^{2+}} \leq n_{th} \\ 0 & \text{if } n_{v_{O}^{2+}} > n_{th} \end{cases}$$  \hspace{1cm} (14)

### 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 $O_{2}^{2-}$ concentration inside the Ti layer. Furthermore we model the transfer of $O_{2}^{2-}$ between the Ti layer and the HfO$_2$ by a flux term at the Ti/HfO$_2$ interface:

$$\Phi = h\left(n_{O_{2}^{2-}}(\text{Ti}) - n_{O_{2}^{2-}}(\text{HfO}_2)\right)$$

where $h$, the transfer coefficient, is modelled by:

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

The transfer coefficient $h$ is thermally activated to take into account the energy needed to break the Ti-O bond 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 $\mu_0$ and $E_{\text{trap}}$ are fitting parameters.

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 (Vpulse) delivering 1.5V during 10$\mu$s. The following electrical biases are applied to the device:

- for reset: $V_s$=Vpulse(t), $V_g$=3V, $V_a$=0V
- for set: $V_s$=0V, $V_g$=1.5V, $V_a$=Vpulse(t)

VI. SIMULATION RESULTS

Reset simulation starts from schematic concentrations of $V_{O}^{2+}$ and $O_{2}^{2-}$ 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 transition is around 4$\mu$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 1789Ω. Low field resistance Roff (after reset simulation) is 48110Ω. Set simulation (Fig.8) starts from concentrations of $V_{O}^{2+}$ and $O_{2}^{2-}$ obtained at the end of the reset pulse (Fig.6c). Low field Ron (after set simulation) is 4149Ω. Roff and Ron 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).
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$_{2+}^{O}$ and oxygen interstitials ions O$^{2-}$ 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.

REFERENCES


