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Stress Induced Vacancy Clustering Mechanism of Resistive Switching in Hafnium Oxides

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ABSTRACT

Reversible changes in the conductivity of HfO₂ dielectric film between high and low resistive states of a metal-insulator-metal memory cell were attributed to the formation of oxygen vacancies and their clustering across the insulator layer. In this study we present an innovative model which includes generation of two-charged states of oxygen vacancies at the anode, their diffusion to the cathode, transformation to one-charged state, and then to neutral vacancies. Vacancy clusters in the insulator layer are built from only neutral vacancies, while the kinetics of the clustering process is controlled by diffusion of mobile one-charged state vacancies. Resistive switching is treated as the formation of critical size vacancy cluster which provides continuous conductive path through the dielectric layer. Good agreement between the experimental data and the theoretical bias and temperature dependences for the delay time was obtained.

INTRODUCTION

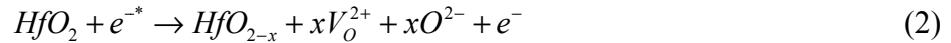
Some electrical insulators display a change in resistance upon application of a bias voltage, a phenomenon named resistive switching (RS). Recently, the RS gained a new interest for fabrication of nonvolatile memories, named resistive random access memories (RRAM). The RRAM technology offers the possibility of reversible changes in the conductivity of a dielectric film between high (HRS) and low (LRS) resistance states by applying voltage pulses of either different or similar polarities to the metal-insulator-metal (MIM) memory cell. While the key factors driving the RS in metal oxides have been identified [1-6], there is no sufficiently developed microscopic description of the conductive pass formation and dissolution which enables memory operations. A sudden drop in resistance in TiO_x and TaO_x crossbar devices has been recently considered as the nucleation of a conductive ordered vacancy phase inclusion, which is characterized by an incubation time with a nucleation barrier inversely proportional to the applied electric field [7]. However, the classical nucleation switching theory cannot describe microscopic details of the conductive pass formation. This study is focused on the microscopic origin of a vacancy enriched conductive filament providing RS in the MIM cells with the HfO₂ oxide insulator.

MODEL

Formation of conductive filament (CF) in HfO₂ is usually considered to be connected with formation of oxygen vacancies and their agglomeration across the insulator layer. Doubly charged vacancies V_o^{2+} can be generated in HfO_{2-x} by oxygen removal at the anode [1]:



or by Fowler-Nordheim injection of energetic electrons at the cathode inducing Hf-O bond breakage [2]:



where e^{-} is an energetic electron. The vacancies V_o^{2+} can capture electrons and transform into singly charged vacancies, V_o^{+} , and neutral ones, V_o^0 . The oxygen ions are formed simultaneously with charged vacancies to provide overall neutrality. Under the electric field the vacancies V_o^{2+} and oxygen ions O^{2-} drift in opposite directions with different velocities. If reaction (1) occurs at the anode, oxygen ions are trapped there while the charged vacancies will move to the cathode direction; opposite situation for the reaction (2) at the cathode. Activation energies for diffusion of oxygen ions and doubly charged vacancies in hafnia are 0.6 eV and 0.7 eV, respectively [3,4], while the activation energy for neutral vacancies is much higher, ≥ 2 eV, and for the V_o^{+} vacancies it is more than 1.5 eV [5]. Conductive path in the dielectric film of HfO_2 can be formed by accumulation of neutral oxygen vacancies [8], or formation of large vacancy clusters, providing metallic properties of the Hf enriched regions.

Let us now describe the main processes occurring in a MIM device resulting in HRS/LRS transition. These processes are depicted schematically in Fig.1.

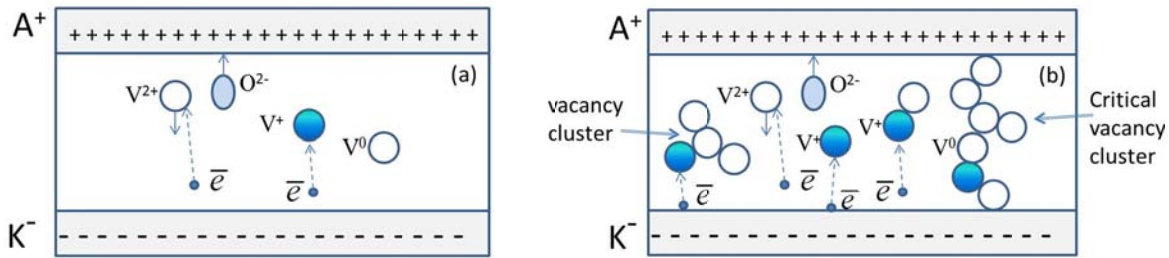


Fig. 1. Generation and transformation of point defects and vacancy clusters in the MIM device under electric bias. Schematic. (a) Two-charged vacancies V_o^{2+} and oxygen ions O^{2-} are created near the anode; the vacancy V_o^{2+} may capture tunneling electrons (TE) and transform to one-charged vacancy V_o^{+} ; the vacancy V_o^{+} can also trap additional TE and transform to a neutral vacancy. (b) Mobile vacancy V_o^{+} can meet neutral vacancy to form a bi-vacancy ($V_o^{+} - V_o$), which then may capture TE and transform to a neutral bi-vacancy ($V_o - V_o$); the vacancy cluster grows by the accession of mobile one-charged vacancies V_o^{+} up to a critical size resulting in the HRS/LRS transition.

The creation of a new oxygen vacancy requires chemical bonds to be broken (oxygen dissociation) and the oxygen ion to be repositioned outside the normal position. Initially, the voltage stress creates doubly charged vacancies and oxygen ions. Within the effective activation energy description [6] bond breakage is considered to be assisted by the local electric field and the temperature around the bond. The corresponding defect generation rate, G , can be approximated by an Arrhenius expression:

$$G = G_0 \exp\left(-\frac{E_a - bF}{k_B T}\right) \quad (3)$$

where F is the applied field, T is the local temperature near the specific oxygen atom, k_B is the Boltzmann's constant, G_0 is a rate constant, which depends on intrinsic material properties, and

b is the bond polarization factor. The vacancies V_o^{2+} are generated near the positive electrode (anode), diffuse to the negative electrode (cathode), where they are stored, possibly after reaction with electrons injected from the cathode, in the form of immobile neutral vacancies. Diffusion equation for the V_o^{2+} vacancies can be written in the following form:

$$\frac{\partial n_V^{2+}}{\partial t} = D_2 \frac{\partial^2 n_V^{2+}}{\partial x^2} - \frac{\partial n_V^{2+}}{\partial x} \bar{V} - \alpha n_f n_V^{2+} + \frac{n_V^+}{\tau_1} \quad (4)$$

where n_V^{2+} is the concentration of V_o^{2+} vacancies, $\bar{V} = 2\bar{e}FD_{V^{2+}} / (k_B T)$ is the drift velocity of vacancies in the electric field F , D_2 is the diffusion coefficient of V_o^{2+} vacancies, $\bar{e} = |e|$ is the electron charge, α is the capture rate of free electrons by vacancy V_o^{2+} traps, n_f is the density of free electrons injected by cathode, and τ_1 is the lifetime of an electron in the one-charged vacancy. The boundary conditions for this diffusion equation are:

$$J_{V^{2+}}(\text{anode}) = J_{V^{2+}}(x=0) = G \quad \text{and} \quad n_V^{2+}(\text{cathode}) = n_V^{2+}(x=d) = 0 \quad (5)$$

If we neglect the last term in eq. (4), one can find the steady-state distribution:

$$n_V^{2+}(x) = 2Ge^{\bar{V}x/2D_2} \left[(\bar{V} + \lambda D_2) e^{\lambda d} - \bar{V} + \lambda D_2 \right]^{-1} \left[e^{\lambda(d-x/2)} - e^{\lambda x/2} \right] \quad (6)$$

where $\lambda^2 = (\bar{V} / D_2)^2 + 4\alpha n_f / D_2$. If we also neglect the following term $\alpha n_f n_V^{2+}$ in eq. (4), then

$$n_V^{2+} = (G / \bar{V}) \left[1 - \exp(-\bar{V}(d-x) / D_{V^{2+}}) \right]. \quad (6a)$$

Vacancies V_o^{2+} may capture electrons tunneling from cathode to the middle part of the dielectric layer (it is described by the term $\alpha n_f n_V^{2+}$ in eq.(4)), and transform to one-charged vacancies V_o^+ , (Fig. 1a) which, in turn, can also trap electrons and transform to neutral vacancies, V_o . Positively charged vacancies cannot form vacancy clusters with each other [8]. Furthermore, we assume, that vacancy clusters of any size may contain no more than single one-charged vacancy, otherwise they decompose. This assumption is justified due to the Coulomb's repulsion energy of two elementary point charges separated by interatomic distance (~ 0.4 nm), which is about 3.6 eV, while the binding energy between lattice vacancies does not usually exceed 0.5 eV [8]. The vacancies V_o^+ and V_o can encounter each other and form a bi-vacancy $V_o^+ - V_o$ (Fig. 1b), which may capture tunneling electron and transform to a neutral bi-vacancy. In turn, the neutral bi-vacancy can meet mobile one-charged vacancy and form 3-vacancy cluster $V_o^+ - V_o - V_o$. The kinetic equations for neutral and one-charged single vacancies

$$\frac{dn_V^+}{dt} = \alpha n_f n_V^{2+} - \frac{n_V^+}{\tau_1} - \beta n_f n_V^+ + \frac{n_V^0}{\tau_0} - \theta n_V^0 n_V^+ + \frac{n_{2V}^{0+}}{\tau_{2V}^{0+}} + \frac{n_{3V}^{0+}}{\tau_{3V}^{0+}} + \dots - \theta n_V^{0-0} n_V^+ - \theta n_V^{000} n_V^+ - \dots \quad (7)$$

$$\frac{dn_V^0}{dt} = \beta n_f n_V^+ - \frac{n_V^0}{\tau_0} - \theta n_V^0 n_V^+ + \frac{n_{2V}^{0+}}{\tau_{2V}^{0+}} + 2 \frac{n_{2V}^{0-0}}{\tau_{2V}^{00}} + \frac{n_{2V}^{000}}{\tau_{3V}^{000}} \dots \quad (8)$$

where β is the capture rate of free electrons by vacancy (V_o^+) traps, τ_0 and τ_1 are the lifetimes of electrons in neutral and one-charged vacancies, τ_{2V}^{00} , τ_{3V}^{000} ... are the lifetimes of neutral vacancy clusters which may decompose by emitting single neutral vacancies, τ_{2V}^{0+} , τ_{3V}^{00+} ... are the

corresponding lifetimes of one-charged vacancy clusters, and θ is the rate of one-charged vacancy cluster formation, $\theta = D_{V^+} / \lambda_1^2$. D_{V^+} is the diffusion coefficient of V^+ , and λ_1 is the jump length of the vacancies. Last terms in eq. (7) correspond to formation of different one-charged vacancy clusters, while last terms in eq. (8) correspond to dissociation of vacancy clusters. Here we assume, that $D_{V^+} \gg D_{V^0}$ [3, 4]. An essential step of large vacancy cluster formation is the neutralization of vacancy clusters: $V^0 - V^+ + \bar{e} \rightarrow V^0 - V^0$. For one-charged and neutral bi-vacancies the kinetic equations are the following:

$$dn_{2V}^{0+} / dt = Q - Pn_{2V}^{0+} + Fn_{2V}^{0-0} \quad (9)$$

$$dn_{2V}^{0-0} / dt = \bar{a}n_{2V}^{0+} - \bar{b}n_{2V}^{0-0} \quad (10)$$

where $Q \equiv \theta n_V^+ n_V^0$, $P \equiv 1 / \tau_{2V}^{0+} + 1 / \tau_{2e}^{0+} + \beta n_f$, $F \equiv 1 / \tau_{2e}^{00}$, $\bar{a} \equiv \beta n_f$, $\bar{b} \equiv (\theta n_V^+ + 1 / \tau_{2V}^{00} + 1 / \tau_{2e}^{00})$, τ_{2e}^{00} is the lifetime to emit electron from a neutral and transform to a one-charged bi-vacancy. The solution of eqs. (9),(10) (assuming n_V^0 and n_V^+ to be constant) are:

$$n_{2V}^{0+} = \bar{n}_{2V}^{0+} \left[\frac{\omega_2}{\omega_1 - \omega_2} \left(1 + \frac{\omega_1}{b} \right) e^{-\omega_1 t} - \frac{\omega_1}{\omega_1 - \omega_2} \left(1 + \frac{\omega_2}{b} \right) e^{-\omega_2 t} + 1 \right] \quad (11)$$

$$n_{2V}^{0-0} = \bar{n}_{2V}^{0-0} \left[\frac{\omega_2}{\omega_1 - \omega_2} (e^{-\omega_1 t} - e^{-\omega_2 t}) + (1 - e^{-\omega_2 t}) \right] \quad (12)$$

where $\omega_{1,2} = (\bar{a}\bar{b} + P) / 2 \pm \sqrt{(\bar{a}\bar{b} + P)^2 / 4 - P\bar{b} + F\bar{a}}$, and \bar{n}_{2V}^{0+} and \bar{n}_{2V}^{0-0} are the stationary concentrations: $\bar{n}_{2V}^{0+} = Q\bar{b} / (P\bar{b} - F\bar{a})$ and $\bar{n}_{2V}^{0-0} = Q\bar{a} / (P\bar{b} - F\bar{a})$. The quasi-stationary concentrations of single vacancies (n_V^0, n_V^+) are extracted in the following way. If the lifetimes of vacancy clusters are large in comparison to the lifetime of single neutral vacancy, τ_0 , then, the quasi-stationary concentration of single neutral vacancies is found from eq. (8) to be

$$\bar{n}_V^0 = (\beta n_f \tau_0) \bar{n}_V^+ / (1 + \theta \tau_0 \bar{n}_V^+) \equiv B \bar{n}_V^+ / (1 + \theta \tau_0 \bar{n}_V^+) \quad (13)$$

where $B \equiv \beta n_f \tau_0$. If $\theta \tau_0 \bar{n}_V^+ \ll 1$, then $\bar{n}_V^0 = (\beta n_f \tau_0) \bar{n}_V^+ \equiv B \bar{n}_V^+$. The quasi-stationary concentration of one-charged single vacancies can be found now from the reduced equation:

$$\alpha n_f n_V^{2+} - \bar{n}_V^+ / \tau_1 - \theta \bar{n}_V^{0-0} \bar{n}_V^+ - \theta \bar{n}_V^{000} \bar{n}_V^+ - \dots = 0. \quad (14)$$

If τ_{2V}^{0+} and $\tau_{2e}^{0+} \gg (\beta n_f)^{-1}$, and, $\tau_{2e}^{00} / \tau_{2V}^{00} \ll 1$ (electron kinetics is much faster than vacancy cluster formation/decomposition), then eqs.(13), (14) are reduced to the following expressions:

$$\bar{n}_{2V}^{0+} = \bar{n}_V^0 (1 + \tau_{2e}^{00} \theta \bar{n}_V^+) / (\beta n_f \tau_{2e}^{00}) \quad \text{and} \quad \bar{n}_{2V}^{0-0} = \bar{n}_V^0. \quad (15)$$

The same is true for stationary higher vacancy clusters' concentrations. For 3-vacancy clusters:

$$\bar{n}_{3V}^{00+} = (1 + \tau_{3e}^{000} \theta n_V^+) \bar{n}_{2V}^{00} / (\tau_{3e}^{000} \beta n_f) = (1 + \tau_{3e}^{000} \theta n_V^+) \bar{n}_V^0 / (\tau_{3e}^{000} \beta n_f) \quad \text{and} \quad \bar{n}_{3V}^{000} = \bar{n}_V^0. \quad (16)$$

Assuming K to be the number of vacancies in the largest stationary clusters, eq. (14) reduces to:

$$\alpha n_f n_V^{2+} - \bar{n}_V^+ / \tau_1 - K \theta B (\bar{n}_V^+)^2 / (1 + \theta \tau_0 \bar{n}_V^+) = 0. \quad (17)$$

For the case $\tau_0 / \tau_1 \ll 1$ (the lifetime of one-charged vacancy is much longer than the lifetime of the neutral vacancy) and $\theta \tau_0 n_V^{2+} \ll 4K$ (the rate of diffusion controlled formation of vacancy clusters is much smaller than the rate of electron emission from neutral vacancies), one can find:

$$\bar{n}_V^+ = (\alpha n_f^{2+} / \beta \theta K \tau_0)^{1/2} \quad \text{and} \quad \bar{n}_V^0 = n_f (\beta \alpha \tau_0 n_V^{2+} / \theta K)^{1/2}. \quad (18)$$

For short times, eqs. (9) and (10) yield the following solutions:

$$n_{2V}^{0+} \approx Q t = \theta n_V^+ n_V^0 t \quad \text{and} \quad n_{2V}^{0-0} \approx Q \bar{a} t^2 / 2 = (\theta n_V^+ n_V^0) (\beta' n_f) t^2 / 2. \quad (19)$$

If concentrations of bi-vacancies are approaching the stationary values which are described in eqs. (15), then for 3-vacancies one obtains for short times:

$$n_{3V}^{00+} \approx \theta n_V^+ n_V^0 t \quad \text{and} \quad n_{3V}^{000} \approx (\theta n_V^+ n_V^0) (\beta' n_f) t^2 / 2. \quad (20)$$

Similarly, for short times, the concentrations of n-V clusters are the following:

$$n_{nV}^{0\dots 0} \approx (\theta n_V^+)^{n-2} (\beta' n_f)^{n-2} n_V^0 t^n / (n)! \quad (21)$$

Let us assume that transition from HRS to LRS corresponds to appearance of a vacancy cluster of a critical size, N . The conductive path for electrons can be formed by N-vacancy cluster with $N \sim d/a$, where a is the interatomic O-O distance in hafnia. Concentration of N-V clusters should reach a certain value, when at least one such cluster appears in the system: $n_{NV}^{0\dots 0} \Delta V = 1$, where ΔV is the volume of hafnia where generation of vacancies occurs. The time needed (the delay time or incubation time) to reach this concentration, t_{RS} , can be found from eqs. (6a), (18), (21):

$$t_{RS} = (N! / \Delta V n_V^0)^{1/N} (\beta / \alpha \beta' n_f)^{1-2/N} (n_V^0)^{-1/N} (2 \bar{e} F \lambda_1^2 K / k_B T)^{0.5-1/N} (D_{V^{2+}} \tau_0 / D_{V^+} G)^{0.5-1/N} \quad (22)$$

DISCUSSION

Equipped with the previous model, we can compare the theoretical dependencies of the delay time with the experimental data available in the literature. Gonon et al. [9] measured the delay time, t_d , of the HRS/LRS transition in Au/HfO₂/Pt stack at a constant voltage stress mode. From the temperature dependence of the delay time they extracted the activation energy ~ 1.05 eV at a bias voltage of +3V, and the bias dependence was approximated by $\exp(-V/V_0)$ with $V_0=0.21$ V [9]. Using eq. (22) yields the activation energy for the transition time t_{RS} :

$$E_{RS} = (E_{V^+} - E_{V^{2+}} + E_a - bF + \Delta E) (N - 2) / 2N. \quad (23)$$

where we assume $\tau_0 \sim \exp(\Delta E / k_B T)$, ΔE is the electron binding energy in the neutral vacancy. Estimation of E_{RS} can be found as follows: the migration activation energies of oxygen vacancies in hafnia are $E_{V^{+}} = 1.5$ eV, $E_{V^{2+}} = 0.7$ eV [3-5], the value of bond energy $E_a = 4.4$ eV [5], and the parameter $b = p_0 \bar{e} (2 + \kappa) / 3$ nm, which was calculated based on the thermochemical description of dielectric breakdown in high dielectric constant materials [10]. For HfO_2 , $\kappa \sim 25$ and $p_0 = 1.02$ for cubic hafnia and $p_0 = 0.44$ for tetragonal hafnia. For the cubic phase one finds $b = 9\bar{e}$ nm, and for the tetragonal phase $b = 4\bar{e}$ nm. Using reasonable values $\Delta E = 0.1$ eV (\sim the relaxation energy around the neutral vacancy with respect to the perfect lattice [11]), and $N = 30$, we obtain $E_{RS} = 0.47 [0.9 + E_a - bV/d] eV$. Next, the voltage bias dependence of the delay time, t_{RS} , is determined by three factors: vacancy generation rate, G , the vacancy drift velocity, \bar{V} , and the density of free electrons injected by the cathode, n_f :

$$t_{RS} \sim (\bar{V} / G n_f)^{1-2/N} \sim (\bar{V} / n_f)^{1-2/N} \exp[-b(N-2)V / 2Ndk_B T] \sim (n_f)^{2/N-1} \exp(-V / V_0(T)) \quad (24)$$

where $V_0(T) = 2Ndk_B T / (b - 2\lambda\bar{e})(N - 2)$. For $b = 9\bar{e}$ nm (as for cubic hafnia), $\lambda = 0.5$ nm, $T = 85^\circ\text{C}$, $d = 10$ nm and $N = 30$, one can obtain $V_0 = 0.083$ V, while using $b = 4\bar{e}$ nm (as for tetragonal hafnia) yields $V_0 = 0.22$ V, very close to the experimental value [9]. If we use the latter value of b , then the Hf-O bond energy should be $E_a = 2.25$ eV to provide activation energy of $E_{RS} = 1.05$ eV for $V = 3$ V. The two times smaller bond energy can be explained by the formation of vacancies at the MI interface, or at the existing point and planar defects in the insulator films.

CONCLUSION

The RS phenomenon was treated as the formation of critical size vacancy cluster which provides continuous conductive path through the dielectric layer. The activation energy of the delay time required to the HRS/LRS transition is a combination of the diffusion activation energies of two- and one-charged vacancies, the binding energy between neutral vacancies, and the activation energy for vacancy generation at the anode. The bias dependence is determined by the vacancy generation rate, the vacancy drift velocity, and the density of free electrons. The available experimental results regarding the temperature and voltage bias dependencies of the delay time are well explained in the frame of the developed model.

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