Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

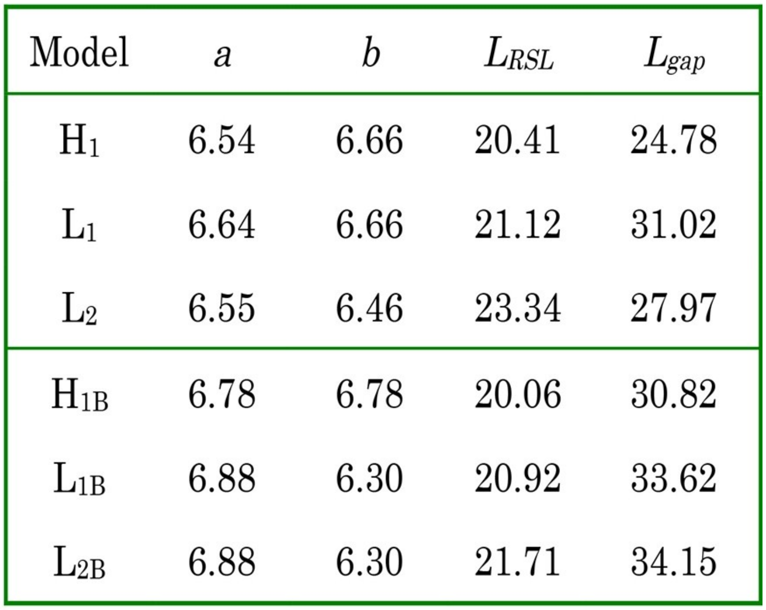
Competitive effects of oxygen vacancy formation and interfacial oxidization on the *ultra-thin* HfO_2-based resistive switching device: Beyond filament and charge hopping models

Hisao Nakamura*, Yoshihiro Asai

National Institute of Advanced Industrial Science and Technology (AIST),
Central 2, Umezono 1-1-1, Tsukuba, Ibaraki 305-8568, Japan

hs-nakamura@aist.go.jp

SI. 1. Structure parameters of the ReRAM cell models



Model	a	b	L_{RSL}	L_{gap}
H_1	6.54	6.66	20.41	24.78
L_1	6.64	6.66	21.12	31.02
L_2	6.55	6.46	23.34	27.97
H_{1B}	6.78	6.78	20.06	30.82
L_{1B}	6.88	6.30	20.92	33.62
L_{2B}	6.88	6.30	21.71	34.15

Table 1. Structure parameters of ReRAM cell models (in Ang unit). The lattice constant, *a* and *b* and the two thickness parameters are listed. L_{gap} is the gap distance between the left and right top electrode surfaces. LRSL is thickness of the RSL, i.e., distance between the most outer Hf layers. The thickness of L_{gap}-L_{RSL} relates to the oxidized interface region.

SI. 2. Construction of effective Hamiltonian and MPSH based on NEGF-DFT

We give a brief note of electronic coupling strength of the target state and states in the electrode, which are obtained by fully first principle NEGF. We first construct Feshbach's effective Hamiltonian. The details of the formalism and the computational procedures are given in the appendix of ref. [1]. We adopted the projected region *P* as the region of the oxidized interface as shown in the manuscript. The left and right outer regions of *P* are denoted as Q_L and Q_R, respectively. In this case, the effective Hamiltonian in the *P*-space near the Fermi level, $H_{PP}^{eff}(\varepsilon_F)$, is represented as

$$H_{PP}^{eff} \approx H_{PP} + H_{PQ_L} G_{QQ}(\varepsilon_F) H_{Q_L P} + H_{PQ_R} G_{QQ}(\varepsilon_F) H_{Q_R P} \tag{S1}$$

where H_{PP} *etc* represent PHP. The term H_{PP} is a standard MPSH and the last two terms of the right hand represent the left (right) self-energies into *P*-space. This effective MPSH is exact, i.e., any states in the the $Q_{L/R}$-space are renormalized through the nonlocal term G_{QQ}. We expand H_{PP}^{eff} by using the PMOs, i.e., eigenstates of H_{PP}. Thank to expansion in the PMO basis, H_{PP}^{eff} is almost diagonal and hence, its element is written as

$$<\varphi_\alpha | H_{PP}^{eff} | \varphi_\alpha >= \varepsilon_\alpha + \frac{i}{2}\gamma_L + \frac{i}{2}\gamma_R, \tag{S2}$$

where the energy of the PMO φ_α is corrected as the sum of eigenvalue of H_{PP}, ε_α^0, and energy- shift by coupling with the electrodes, i.e.,

$$\varepsilon_\alpha = \varepsilon_\alpha^0 + \mathrm{Re} < \varphi_\alpha | H_{PQ_L} G_{QQ}(\varepsilon_F) H_{Q_L P} + H_{PQ_R} G_{QQ}(\varepsilon_F) H_{Q_R P} | \varphi_\alpha >. \tag{S3}$$

The terms $\gamma_{L/R}$ are the transfer coupling with the PMO on the molecule and outer left/right regions,

$$\begin{aligned} \gamma_L &= 2\,\mathrm{Im} < \varphi_\alpha | H_{PQ_L} G_{QQ}(\varepsilon_F) H_{Q_L P} | \varphi_\alpha > \\ \gamma_R &= 2\,\mathrm{Im} < \varphi_\alpha | H_{PQ_R} G_{QQ}(\varepsilon_F) H_{Q_R P} | \varphi_\alpha > \end{aligned}, \tag{S4}$$

respectively. Since we selected the oxidized interface on left (or right) side as *P* space in the present case, we need to consider only γ_L (or γ_R) to identify electronic coupling strength of the interface in the RSL with the electrode.

1. Nakamura, H., et al., "*Conducting orbital switching by bias-induced electronic contact asymmetry in bipyrimidinyl-biphenyl diblock molecular diode." J. Phys. Chem.* C. **115** 19931 (2011)

SI. 3. LOE formulation and analysis of resistance by single level model

Inelastic electric current by electron-phonon interactions is calculated by the same NEGF scheme as that for ballistic current, where retarded (Σ_{eph}) and lesser ($\Sigma_{eph}^{<}$) self-energy terms can be evaluated by Born expansion as follows:

$$\begin{aligned}\Sigma_{eph}(E) = &\frac{i}{2\pi}\int d\omega \left\{D_{\alpha}^{<}(\omega)M^{\alpha}G^{\dagger}(\varepsilon-\omega)M^{\alpha} + D_{\alpha}^{\dagger}M^{\alpha}G^{>}(\varepsilon-\omega)M^{\alpha}\right\} \\ &-\frac{i}{2\pi}\int d\omega \left\{D_{\alpha}(0)M^{\alpha}\mathrm{Tr}\left[\mathrm{G}^{<}(\omega)M^{\alpha}\right]\right\}\end{aligned} \tag{S5}$$

$$\Sigma_{eph}^{<}(E) = \frac{i}{2\pi}\int d\omega \left\{D_{\alpha}^{<}(\omega)M^{\alpha}G^{<}(\varepsilon-\omega)M^{\alpha}\right\} \tag{S6}$$

where the label α represents the normal mode whose eigen frequency is Ω_{α}. Here we use atomic unit. M^{α} is electron-phonon coupling matrix as given in the manuscript. *G* and *D* are electron and phonon Green's function, respectively. In the present study, we omit nonequlibrium part of phonon Green's function i.e., $D^{<}$ is in thermally equilibrium. Note that *G* (and $G^{<}$) generally includes $\Sigma_{eph}^{(<)}$ terms. In the lowest order expansion, the Green's functions are given as

$$G = G_0 + G_0\Sigma_{eph}G_0 \tag{S7}$$

$$G^{<} = G(\Sigma_{L}^{<} + \Sigma_{R}^{<} + \Sigma_{eph}^{<})G^{\dagger} \tag{S8}$$

where G_0 is the retarded Green's function without electron-phonon interaction, i.e., it is used to calculate ballistic current: thus inelastic current is expressed by using G_0 directly. Though the rigorous form is given in e.g., ref [2], it is still impractical for full first-principles calculation due to computational difficulties. When there is no narrow resonance close to the Fermi level and/or many numbers of phonon modes are included in the calculation, rigorous LOE is further simplified as shown in ref [3]. The inelastic electric current term by the conventional LOE is give as

$$\delta I = \sum_{\alpha}\delta I_{\alpha} = \int dE J_{\alpha}(E) \tag{S9}$$

$$J_\alpha(E)=\frac{1}{\pi}\{T_\alpha^{ec}(2N_\alpha+1)(f_L-f_R)+2T_\alpha^{ecL}(f_{L+}-f_{L-})(f_L-f_R)+2T_\alpha^{ecR}(f_{R+}-f_{R-})(f_L-f_R)\}$$
$$+\frac{1}{\pi}T_{\alpha+}^{in}\{N_\alpha(f_L-f_{R+})-f_{R+}(1-f_L)\}+\frac{1}{\pi}T_{\alpha-}^{in}\{N_\alpha(f_L-f_{R-})-f_L(1-f_{R-})\} \qquad \text{(S10)}$$

$$T_\alpha^{ec}(E)=2\,\mathrm{Re}\,\mathrm{Tr}[M^\alpha G_0(E)M^\alpha G_0(E)\Gamma_R(E)G_0^\dagger(E)\Gamma_L(E)G_0(E)] \qquad \text{(S11)}$$

$$T_\alpha^{ecL/R}(E)=\mathrm{Im}\,\mathrm{Tr}[M^\alpha G_0(E)\Gamma_{L/R}(E)G_0^\dagger(E)M^\alpha G_0(E)\Gamma_{R/L}(E)G_0^\dagger(E)\Gamma_{L/R}(E)G_0(E)] \qquad \text{(S12)}$$

$$T_\alpha^{in}(E)=\mathrm{Tr}[G_0(E)M^\alpha G_0(E)\Gamma_R(E)G_0^\dagger(E)M^\alpha G_0^\dagger(E)\Gamma_L(E)] \qquad \text{(S13)}$$

where $f_{L/R}$ is the Fermi-Dirac function whose chemical potential $\mu_{L/R}$ is that of the left/right electrode, (i.e., difference of chemical potential is equal to bias.), and N_α is Bose-Einstein distribution function of Ω_α. The function $f_{L\pm}$ represents the Fermi-Dirac function where the chemical potential is $\mu_L\pm\Omega_\alpha$. $\Gamma_{L/R}$ is $i(\Sigma_{L/R}-\Sigma_{L/R}^\dagger)$, and $\Sigma_{L/R}$ is left (right) lead self-energy. We calculated Eqs (S9)-(S13) by NEGF-DFT to evaluate inelastic current and relating derivative resistance. In the single level model, G_0 has a simple form, $\frac{1}{(E-\varepsilon_a+i\gamma)}$, where we rewrote the coupling of the single level of the RSL and left/right electrodes as $\gamma=\Gamma_L/2=\Gamma_R/2$. In the low bias regime, G_0 is further approximated as $\frac{1}{(E_F-\varepsilon_a+i\gamma)}$ while energy dependence of the terms such as (f_L-f_R) in Eq (S10) should be explicitly considered in the integral. Then we obtain Eq. (1) in the manuscript immediately. Furthermore, since the transmission coefficient is given as $\tau(E)=\frac{\gamma^2}{(E-\varepsilon_a)^2+\gamma^2}$, Eq. (1) is proportional to $\tau(1-2\tau)$.

2. Viljas, J. K et al. "Electron-vibration interaction in transport through atomic gold wires." *Phys. Rev. B.* **72** 245415 (2005)

3. Nakamura, H., et al., "Efficient ab initio method for inelastic transport in nanoscale devices: Analysis of inelastic electron tunneling spectroscopy" *Phys. Rev. B.* **78** 235420 (2008)

SI. 4. Evaluation of the activation energy by charge trap model

In the Figure (S1), we show the calculated potential energy profile by hopping the charge trapping on (V_o^- state) along the charge transfer (CT) coordinate (black triangles), which is based on the charge trap model as decoherence limit. The solid and dot red lines represent the Marcus parabola of donor (i.e., initial state) and acceptor (i.e., final state) of the trapped charge on the V_o site, respectively. The parabolas are obtained by fitting the calculated potential energy profile. The activation energy is estimated by energy of the crossing point of the two parabolas, i.e., *ca*. 2.6 eV. Because of no negligible avoided crossing effect, effective activation energy may reduce to 0.6 eV as adiabatic limit. The evaluated coupling between the donor and acceptor states is 1.0 eV.

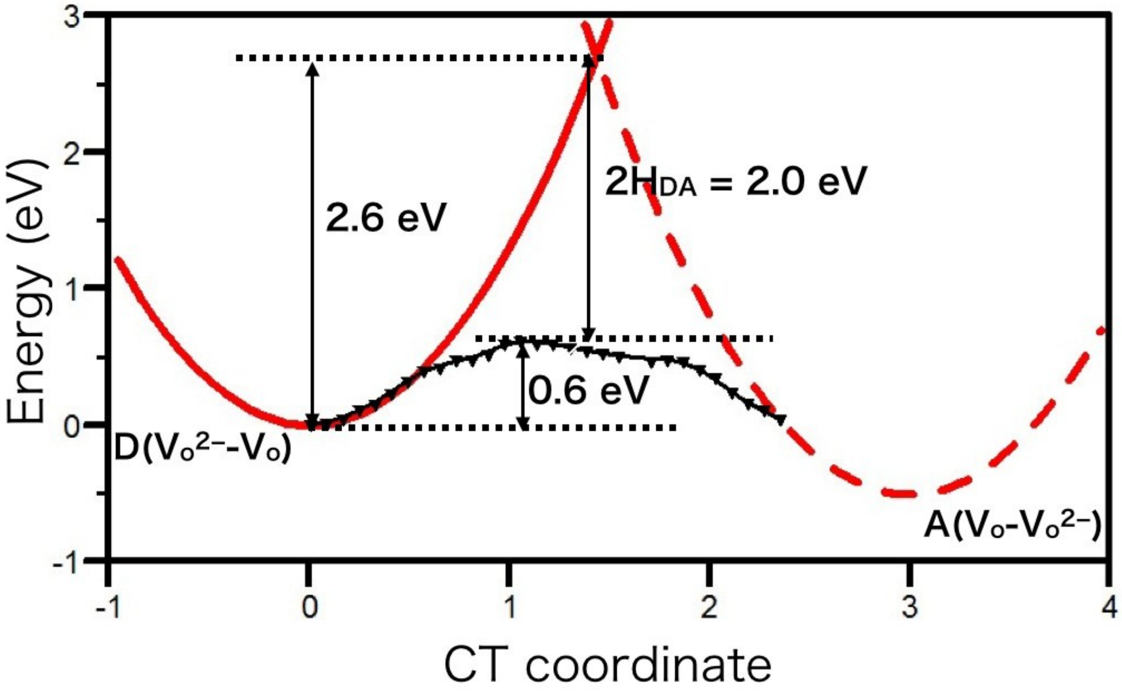


Figure (S-1). The evaluated Marcus Parabola.