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Transport Physics Mechanisms in Thin-Film Oxides

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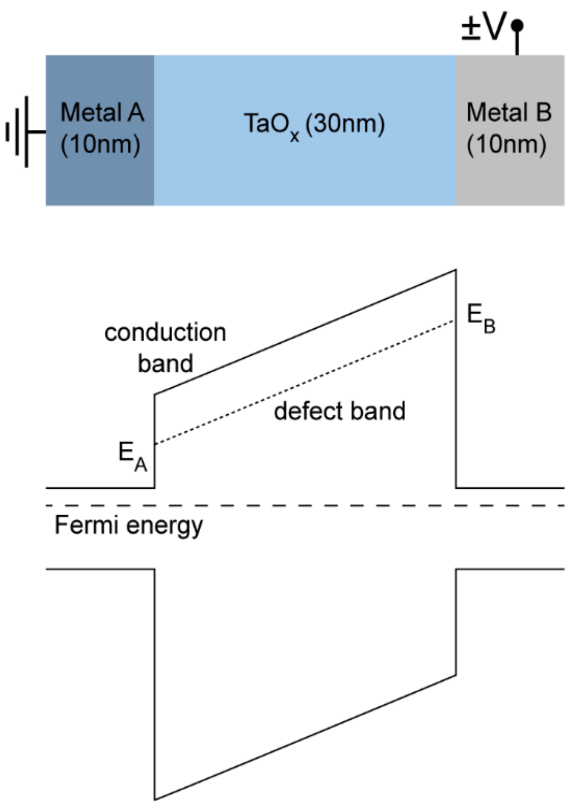
Metal-Insulator-Metal (M-I-M) Structures

Prototypical Structure:



M-I-M Thin Film Oxides of Great Technological Interest

- Oxide Based Capacitors
- Prototypical RRAM Devices

Simplified asymmetric structure zero-bias band diagram:

Band offsets between metal A and metal B electrodes and the oxide are assumed to be 1.0eV and 1.5eV, respectively.

Symmetric system also considered (1.0eV offsets for each electrode)

However… The Details of the Transport Mechanisms Are Not Well Understood!

Motivation For Developing a Unified Model

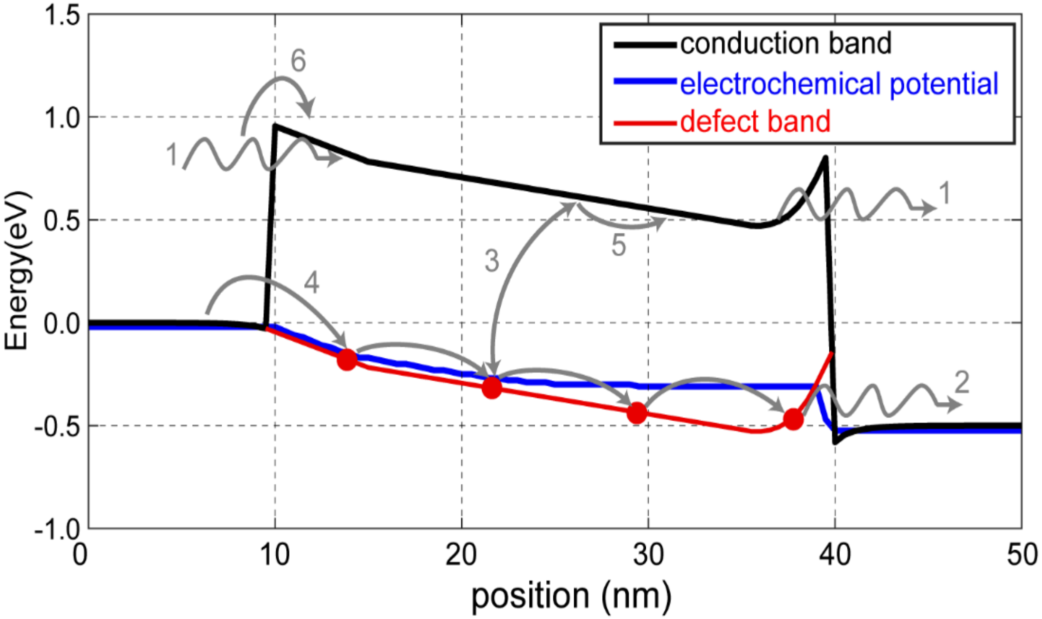
•**Relative strength of various transport mechanisms not well understood, despite decades of research**

•**Most theoretical understanding has come from fitting individual analytical expressions to experimental data**

•**Combining all relevant mechanisms into a *unified model* provides great insight:**

→**Helps understanding switching behavior in bipolar RRAM devices**

→**Important for understanding leakage current mechanisms in oxide-based capacitors**



(1,2) Band / band tunneling
(3) Cond. /defect band electron emission-capture
(4) Defect band hopping
(mean hopping distance exaggerated for clarity)
(5) Conduction band drift-diffusion
(6) Thermionic emission

REOS Formalism

REOS: *Radiation Effects in Oxides and Semiconductors* computer code -- Reactive transport with heat equations for the electrons, holes and the lattice

Transport Kinetic Equation:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathrm{J}_i + \sum_j \nu_{ij} R_j + G_i$$

Drift-Diffusion equation:

$$\mathrm{J}_i = q c_i \overline{\mu}_i \nabla \phi + D_i \nabla c_i$$

Defect Chemistry Included in Model:

$$V^+ + e \leftrightarrow V^0$$

$$\nu_{n1} R_1 = k_{1f} \left[V^+\right] n - k_{1r} N_{th} \left[V^0\right]$$

$$k_{1f} = \sigma \nu_{th} e^{-E_f/kT} \quad k_{1r} = \sigma \nu_{th} e^{-E_r/kT}$$

J_i = Current density of species i

ν_{ij} = Reaction coef. for reaction j

R_{ij} = React. rate coef. for species i in reaction j

G_i = Species gen. rate (non-reactive event)

q = Coulomb charge

c_i = Species concentration

$\overline{\mu}_i$ = Species mobility

ϕ = Electric potential

D_i = Diffusion coefficient

REOS Formalism (cont.)

Metal-Oxide Interface Tunneling Mechanisms:

- Free band-Free band
- Free band- defect site

WKB Method is used to determine the local species generation rate about an interface for each mechanism. Energy levels are adjusted appropriately for each mechanism.

$$J_T(z_1,z_2)=\frac{qm^*k_BT}{2\pi^2\hbar^3}\int_0^\infty dE\,T(z_1,z_2,E)\left\{\ln\left(1+e^{(\mu_1(z_1)-E)}\right)-\ln\left(1+e^{(\mu_2(z_2)-E)}\right)\right\}$$ Tsu-Esaki Formula

WKB transmission probability (classical turning points z_1, z_2):

$$T(z_1,z_2,E)=\exp\left(-2\int_{z_1}^{z_2}\kappa(z)dz\right) \qquad \kappa(z)=\sqrt{\left(2m^*/\hbar^2\right)\left(E_c(z)-E\right)}$$

$$\Rightarrow G(z_2)=\frac{1}{q}\nabla\cdot J_T(z_1,z_2)$$ Carrier Generation within Drift-Diffusion formalism

REOS Formalism (cont.)

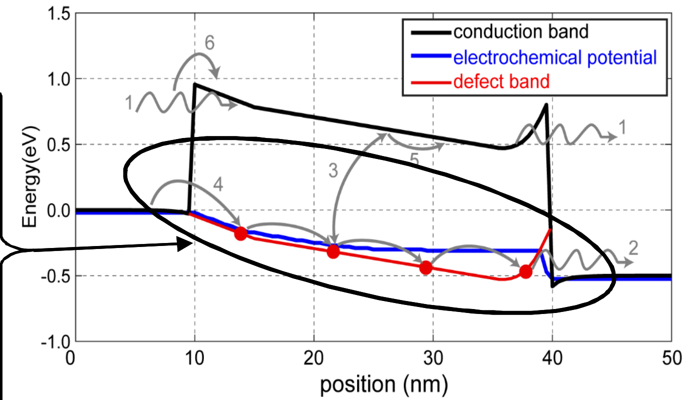
REOS Hopping Mechanism

Hopping occurs as a series of implied tunneling events between adjacent lattice sites.

Kinetic equation:

$$\frac{\partial N^*(R_n)}{\partial t} = \Omega W_0 \exp(-2\alpha\Delta)\times$$

$$\begin{Bmatrix} H(E_{nL})N^0(R_n)N^*(R_{n-1}) - H(-E_{nL})N^0(R_{n-1})N^*(R_n) + \\ H(E_{nR})N^0(R_n)N^*(R_{n+1}) - H(-E_{nR})N^0(R_{n+1})N^*(R_n) \end{Bmatrix}$$



N^* = density of occupied sites

N^0 = density of unoccupied sites

Reaction rate terms:

$$E_{nL} = E_n - E_{n-1}$$

$$E_{nR} = E_{n+1} - E_n$$

$$H(E) = \exp(-E/kT) \quad E \geq 0$$

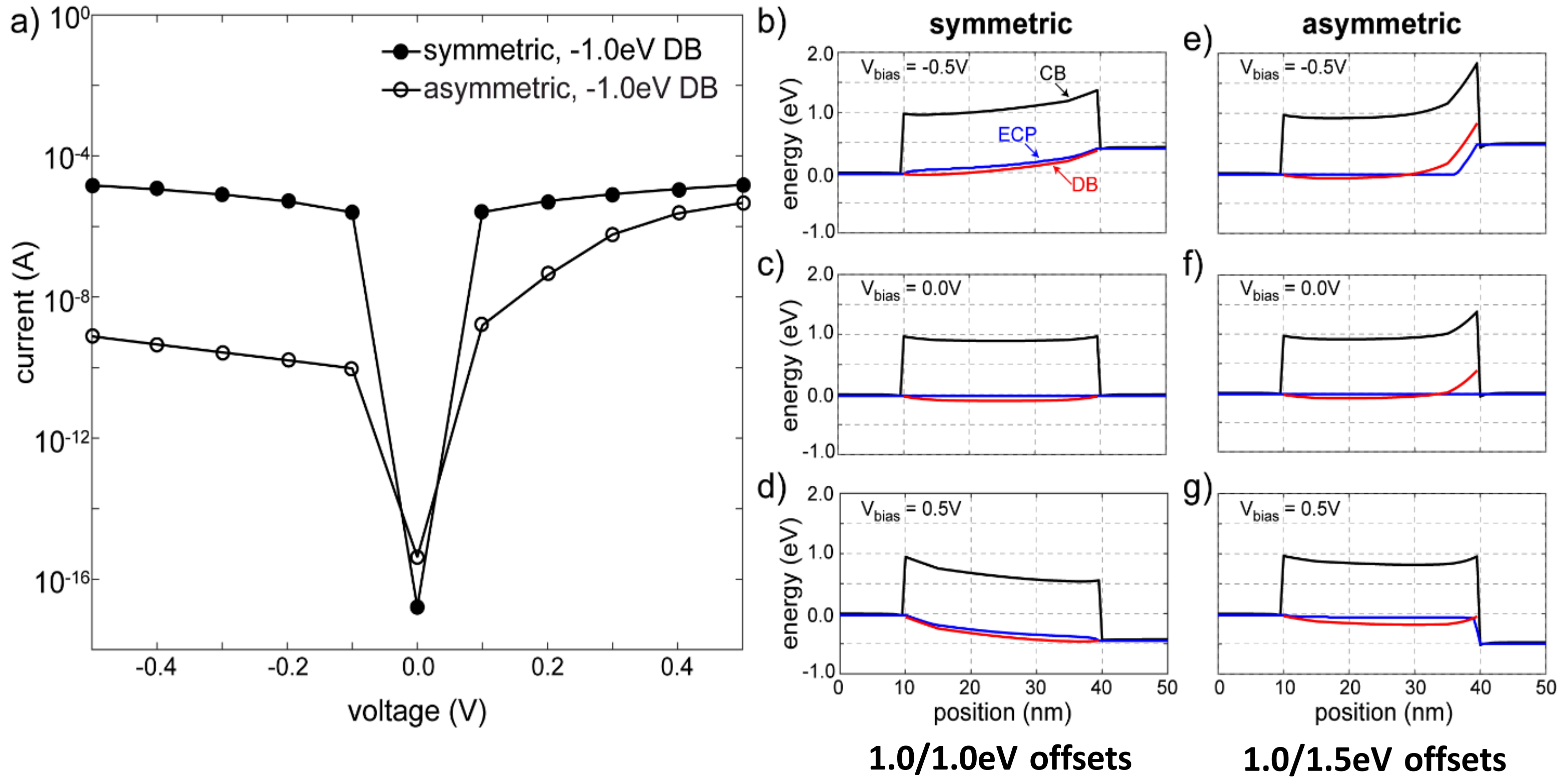
$$H(E) = 1 \quad E < 0$$

$$\Omega = \alpha^{-2}\Delta = \alpha^{-2}\frac{(R_{n+1} - R_{n-1})}{2}$$

α^{-1} = localization length that defines tunneling ≈ 0.1 nm

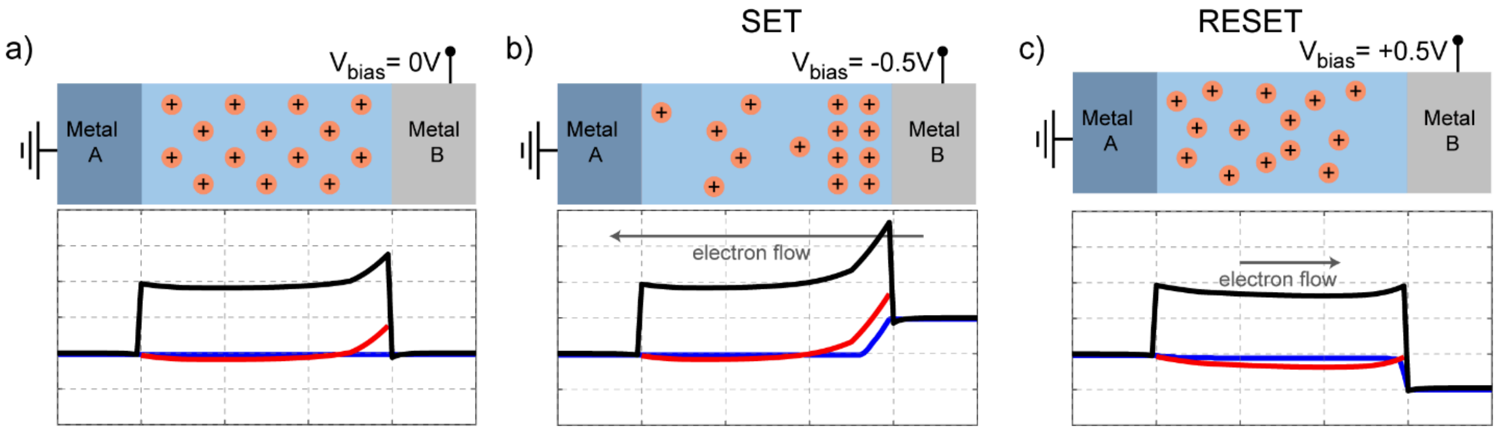
$W_0 \approx 10^{13}$ Hz

REOS Study: Symmetrical vs. Asymmetrical Devices
- Using all Aforementioned Transport Mechanisms Except Joule Hearing -



- **Uniform initial density of neutral vacancies (1.0 x $10^{19}/cm^3$)**
- **Positive bias → Thermionic current dominates in both devices → Similar I-V at higher voltages**
- **Negative bias → Device I-V limited by tunneling at the 1.5eV electrode for asymmetric devices.**
- **Results qualitatively consistent with work of Wang & Zhou (Nanoscale, 2015, Vol. 7)**

Asymmetrical Device: Understanding Vacancy dynamics and Tunneling



The asymmetric band structure profiles of the previous figure, but with but with a visualization of the vacancy motion and concentration under bias.

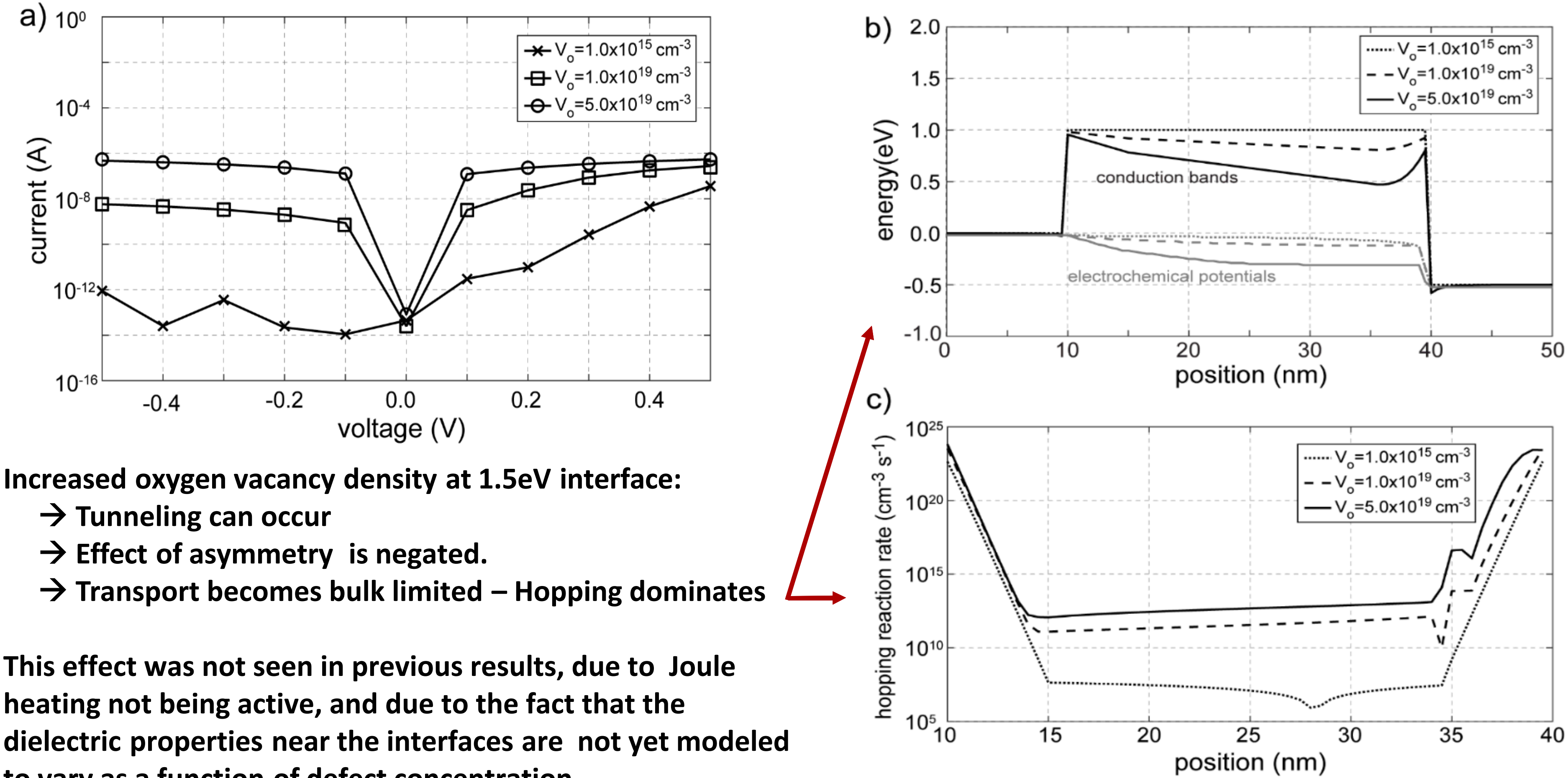
- Negative bias on 1.5eV electrode → vacancies drift toward 1.5eV electrode.
- Electron current is opposite to this direction → Joule heating is strongest on opposite side
- Diffusion of vacancies away from the 1.0eV electrode (thermal process) and drift in Field

  →Strong accumulation of vacancies near the 1.5eV electrode.
- Results in a low-resistive on-state.
- Reset by applying bias of opposite polarity.

This indicates a mechanism for Bipolar RRAM switching!

Asymmetrical Device:
REOS Study: Variation of Defect Density near 1.5eV Barrier

Manual increase of vacancy concentration near 1.5eV electrode indicates supports the hypothesis. Occurs in actuality by Joule heating.



Increased oxygen vacancy density at 1.5eV interface:

- → **Tunneling can occur**
- → **Effect of asymmetry is negated.**
- → **Transport becomes bulk limited – Hopping dominates**

This effect was not seen in previous results, due to Joule heating not being active, and due to the fact that the dielectric properties near the interfaces are not yet modeled to vary as a function of defect concentration.

Conclusion

- REOS model provides a hypothesis of switching in M-I-M system of technological interest: A prototypical RRAM device.

- REOS model provides insight regarding insight vs. bulk limited current in M-I-M systems.

- Unified electronic computational model (REOS) is In qualitative agreement with analytical fit To experimental data.

- Future work to include Joule heating effects and varying insulator properties as a function of vacancy concentration.

Thank You!

Questions?