Prospects and Challenges of Redox-based RRAM Concepts

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Outline
1. Introduction
2. Electrochemical metallization effect
   - cation migration redox systems
3. Valence change switching effect
   - anion migration redox systems
4. Thermochemical switching effect
5. Conclusion

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Introduction

Basic Definitions of Resistive RAM

Operation
- Electrical switching between ON(LRS) and OFF(HRS) state
  - often an initial electrical formation (defined stress) needed
  - "write"-operation by large voltage pulses
    (typically with current compliance)
  - "read" operation by small (sensing) voltage pulses

Polarity modes of RRAM

Unipolar (symmetrical) - URS
- SET
- RESET
- Read
- CC

Bipolar (antisymmetrical) - BRS
- SET
- RESET
- Read
- CC

History
- many reports since the 1960s
- mainly binary oxides, mainly unipolar switching
- Stan Williams et al. (2008):
  memristor / memristive devices according to L. Chua
Emerging Memories: Classification of the mechanisms

Resistive Switching Memories

- Nanomechanical Memory
- Molecular Configuration Memory
- Phase Change Memory
- Electrostatic / FE Effects
- Phase Change Effect
- Valency Change Effect
- Electrochemical metatization cell
- Electrochemical Effects
- Electrostatic / FE Effects
- Ferroelectric / MF Effects
- Magnetic Memory Effects

Emerging Memories: Classification of the mechanisms

Resistive Switching Memories

- Nanomechanical Memory
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Redox-based switching phenomena in chalcogenides
Confinement of the Switching Event

Important issue
Location of the switching event - In the electrode area

- effect confined to filaments?
- homogeneously distributed effect?

Waser & Aono, Nat. Mat. (2007)
A. Sawa, Mat. Today (2008)

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Electrochemical metallization switching
- Cation-migration induced redox systems
Electrochemical Metallization Memory

Names: Electrochemical Metallization Memory (ECM); PMC; CBRAM

Operation
- **ON-switching:** Reduction @ cathode
  - Ag filament formation
  - \( Ag^+ + e' \rightarrow Ag \)
  - M. Faraday (1834)
- **OFF-switching:** Oxidation @ anode
  - \( Ag \rightarrow Ag^+ + e' \)

Electrolyte
- * amorphous GeSe\(_{2+x} \) and GeS\(_{2+x} \)
- * Disordered and amorphous sulfides and oxides

SiO\(_2\) – an unconventional ECM electrolyte

States and Processes
Looking at the elementary steps

C. Schindler et al. (2007)
ECM operation – in search of the rate-limiting step

**Anodic dissolution**
- electrochemical electron transfer reaction (Butler-Volmer)
- no overpotential expected

**Cation transport**
- drift /diffusion transport
- high fields → drift dominant

**Cathodic deposition**
- electrochemical electron transfer reaction (Butler-Volmer)
- crystallization overpotential expected

**Filament growth**
- one “winning” filament, because of field confinement

Formation process

- significantly higher SET voltage
- thickness dependence of SET voltage

→ drift is rate-limiting during formation
→ drift is not(!) rate-limiting during switching

C. Schindler et al. (2008)
ECM operation – in search of the rate-limiting step

Kinetics of the SET process for Cu / SiO2(15nm) / Ir cells

- SET voltage $V_{on}$ depends exponentially on $1/ramp$ rate (over > 8 orders of magnitude!!)
- a threshold voltage exists

$\rightarrow$ **RRAM application**: guarantees fast switching and long retention times

$\rightarrow$ **Understanding** process is cationic electron transfer reaction limited!

C. Schindler et al. (2008)

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ECM operation – in search of the rate-limiting step

Kinetics of the cathodic reaction

1. possibility: Electron transfer

Butler-Volmer-equation

$$i = i_0 \left[ \exp \left( \frac{\alpha z e \eta}{kT} \right) - \exp \left( \frac{(1-\alpha)z e \eta}{kT} \right) \right]$$

2. possibility: nucleation overpotential

$$i = K (Z_0, N_c) \exp \left( \frac{(N_c + \alpha) z e \eta}{kT} \right)$$

$Z_0$: areal density of nucleation sites

$N_c$: number of atoms of a critical nucleus

C. Schindler et al. (submitted)
**ECM – Molecular Dynamics Modeling**

\[
\begin{align*}
\nu_i(t=0) & \text{ distributed uniformly} \\
\nu_i(t=0) & = \Delta v_i^0 \\
\nu_i(t=0) & = \frac{2eE_{\text{plate}}}{m_{\text{Cu}}} \\
\end{align*}
\]

Compute location \( x_i \)

\[
\begin{align*}
x_i(t+\Delta t) & = x_i(t) + \frac{1}{2}v_i(t) + \frac{1}{2}a_i(t) + \frac{1}{2}a_i(t+\Delta t) \\
\end{align*}
\]

compute forces on ions

\[
\begin{align*}
q_i(t+\Delta t) & = q_i(t) - \frac{2e}{m_{\text{Cu}}} \cdot \sum_{j \neq i} F_{\text{Coulomb}} \\
\end{align*}
\]

Compute velocity \( v_j \)

\[
\begin{align*}
F_{\text{Coulomb}} & = q_i \cdot q_j / r_{ij} \\
F_{\text{electric}} & = q_i \cdot E \\
F_{\text{magnetic}} & = q_i \cdot B \\
\end{align*}
\]

\[
\begin{align*}
\dot{v}_j(t+\Delta t) & = \frac{1}{m_{\text{Cu}}} \left( \sum_{i \neq j} F_{\text{Coulomb}} - \sum_{i \neq j} F_{\text{electric}} - \sum_{i \neq j} F_{\text{magnetic}} \right) \\
\end{align*}
\]

\[
\begin{align*}
n & = \frac{q_i^2}{2 \pi e \epsilon_0} \\
\end{align*}
\]

**ECM operation – RESET issue**

**Location of the RESET event**

After SET \( \rightarrow \) metal filament (e.g. Ag)  
RESET \( \rightarrow \) where will the filament will open?  
Experimental / theoretical finding:  
at Ag filament / Ag electrode contact

**General question**

Situation after RESET – chemically symmetrical cell!  
How can a symmetrical cell switch in a bipolar fashion?  
**Possible answer** \( \Rightarrow \) Morphological effect (?)  
Impact on long-term reliability (?)

**Example:**  
Ag filament of 10nm diameter at \( I = 1 \mu A \)  
\( \dot{h} \approx 1.3 \text{ m/s} \)

**Growth speed of a (cylindrical) nanofilament**

\[
\dot{h} [\text{cm/s}] = \frac{M_\Delta}{\pi r^2 z N_A e_i \rho} I [\text{A}] 
\]

**Example:**  
Ag filament / Ag electrode contact

**RESET**  
b) late ON-state  
c) Early OFF-State  
V = 200mV  
(steps 10 mV)

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Valence change switching
- anion-migration induced redox systems

Examples
Capacitor-like structure with
► Cr-doped SrZrO$_3$ thin films
► PCMO thin films
► (Ba,Sr)TiO$_3$ thin films
► TiO$_2$ thin films
► SrTiO$_3$ Single crystals as resistive element

Characteristics
after forming process: reversible bipolar switching between stable impedance states

Basics of ionic defects and valencies of SrTiO$_3$

Point defects in compensated SrTiO$_3$ (calculated)

HT: annealing at a High Temperature equilibrium (e.g. 1000 K)
LT: quenching (at each point) to a Low Temperature (e.g. 400 K)

Basics of ionic defects and valencies of SrTiO$_3$

HT conductivity of epi-SrTiO$_3$
PLD grown thin films

C. Ohly et al., JAmCerSoc (2006)
Extended defects in SrTiO$_3$ & their electronic structure

- Grain boundaries and their impact on conductivity

R. Hagenbeck et al. (1999)

Extended defects in SrTiO$_3$ & their electronic structure

- Low angle grain boundaries ...
  - Perl chains of dislocations

R. De Souza et al. (2003)

Dislocations ...
  - Made visible by etch pits on the surface

K. Szot (2007)
Edge dislocations in SrTiO$_3$ crystal (stacking fault)

Jia et al. PRL. (2006)

Thermal preformation by reduction annealing:
conductive Tip AFM Mapping – types of I-V Characteristics

SrTiO$_3$ s.c. thermally reduced at 850 $^\circ$C, pO$_2$ ~ 10$^{-20}$ bar

Extended defects in SrTiO₃ & their electronic structure

Dislocation exit ...

... at a center of an etch pit is highly conducting (1)

- Surface chemically etched
- Reduction anneal at 1000 K
- Simultaneous AFM topography and LC-AFM current scan

K. Szot (2008)

Emulating the formation in homogenous SrTiO₃

Electrochemical concentration polarization

... based on drift-diffusion in STO:Fe as a mixed ionic-electronic solid electrolyte Pt/STO:Fe/Pt cell

... for low polarization voltages

Analytical solution for \( t \to \infty \)

\[
\frac{\partial n}{\partial x} = \frac{2eV}{\partial x} \left( \frac{V_i}{V} \right)
\]
Emulating the formation in homogenous SrTiO$_3$

Electrochemical concentration polarization
... based on drift-diffusion in STO:Fe as a mixed ionic-electronic solid electrolyte Pt/STO:Fe/Pt cell

... for higher polarization voltages

1-D numerical calculation assuming partially ion blocking electrodes

Results:
• extremely pronounced $V_c$ concentration polarization
• enhanced n-conductivity near the cathode
• enhanced p-conductivity near the anode
• extension of the regions depends on the blocking coefficients

Waser et al. (1990)

Emulating the formation in homogenous Pt/STO:Fe/Pt

Concentration polarization
- made visible by electrocoloration
true color transmission pictures of a STO:0.3at Fe crystal slab

Time

Waser et al. (1991)
Emulating the formation in homogenous Pt/STO:Fe/Pt

Concentration polarization - made visible by electrocoloration
.... and simulated increase in the overall conductance

Time

Waser et al. (1991)

Microscopic view on electrocoloration / formation

Optical micrograph and CAFM (above) and AFM tapping mode (right)

Tip-induced switching of dislocations in SrTiO$_3$


I-source
I-const
Electrometer

Electroreduction
SrTiO$_3$ (100)
$T=450^\circ$C, $I_{\text{const}}=1$ mA
Vacuum

R (Ω)

U (V)

0.0 0.5 1.0 1.5 2.0

0.0 1.0 2.0 3.0 4.0

300 600 900 T (K)

50nm
3nm
0nm

50nm
3nm
0nm

10$^6$ 10$^8$ 10$^{10}$ 10$^{12}$

3.2 × 10$^6$ Ω
1.4 × 10$^{10}$ Ω

0 40 80 Distance (nm)

200 400 600 800 1000 Current (nA)

0 1 2 3 4 5 Applied bias (V)
Switching of epitaxial STO (10nm) thin films

LC-AFM write/erase processes on epi-STO (10nm) / SRO / STO

R. Dittmann, K. Szot, R. Waser
rrl-pss, 2007

Redox reaction at the electrode

Extended defects after electroreduction

Formation of localized metallically conducting sub-oxides by electroreduction
Redox reaction at the electrode

- Interconnected network of extended defects
- Switching ON – oxygen vacancy accumulation near the surface; conduction through the Ti(4-x)+ sublattice


Switching of SrTiO$_3$ (100), Potential distribution
RT, $p=10^{-8}$ mbar

K. Szot, to be published
Electroded epi-SrTiO3 thin film

System (example)

Pt top electrode

Schottky contact

epi-STO (750nm) ohmic contact

Nb-STO substrate

Forming

Formation of a virtual cathode

Menke et al. (2008)

Impedance spectroscopy

Switching

• Reversible switch between two formed states (ON / OFF)

• Contact point of conductive filament is modified by voltage-driven accumulation / dispersion of

Redox-based Oxide Memory – Write time < 10 ns

Pt/TiO2(40nm)/Pt cells prepared by e-beam lithography and lift-off technique

Nauenheim, Kügeler, Waser, (submitted)
Switching model – recent results

Pt/TiO2(27nm)/Pt stack, sputter deposited, electroformed at 1mA for BRS operation

HP Memristor – asymmetry by graded system


D. Strukov, J. Borghetti, R. S. Williams, Small (2008. accepted)
4 Thermochemical Switching Effect

Materials
MIM thin film stack with I = transition metal oxide showing a slight conductivity
  e. g. Pt/NiO/Pt

SET process
Controlled dielectric breakdown
  e. g. by thermal runaway
  ⇒ formation of a conducting filament

RESET process
Thermal dissolution of the filament (fuse blow)
  ⇒ disconnected filament

I. G. Baek et al.
(Samsung Electronics), IEDM 2004
**Temperature profile - Thermal effect assisting other switching types?**

FEM simulation (Ansys®) of metallic TiO filament (3 nm) in TiO2 matrix

- 1 filament
- 3 filaments

**Relationship to other switching effects**

Toggle between bipolar and unipolar switching has been possible by adjusting the current compliance; demonstrated for TiO2 thin films (Jeong et al. 2006) and Cu:TCNQ (Kever et al. 2006)

High current compliance ⇒ unipolar fuse/antifuse switching

**FEM Simulation of the RESET process**

160 nm thick NiO film on n-Si with Au top electrodes

*U. Russo et al., IEDM 2007*
5 Conclusions

Prospects

- Ultimately high scaling potential
  ... of both, cation- and anion-migration memristive concepts
- Functions beyond pure memory
  ... from FPGA type logic to neural functions
- Technologically compatible to CMOS interface

Challenges

- Highly scaled interconnect lines
  ... and reliable electrode contacts
- Long-term reliability
  ... in particular with respect to retention (at 85 °C)
- Design rules not yet known
  ... to guide search in the material’s „treasure map“
- Defect engineering
  ... just at ist very beginning
Redox-based nanoscale memristors – defect engineering?

Aim: tailoring structural filaments

2D dislocation effects on resistive switching

Sr$_2$TiO$_4$ / SrTiO$_3$

Vicinal surface: dislocation density controlled by a miscut angle of substrates.

Anti-phase boundaries (APBs) as dislocation centers working as conduction filaments ??

.. inspired by ...

ex.: Bi$_4$Ti$_3$O$_{12}$/SrTiO$_3$

APL83, 2315

Thank You!
Bipolar resistive switching in transition metal oxides

Purely electronic charge trap mechanism?

Pt/STO(50nm)/Pt, V =1V, 300 K

General result

No trap site suitable to match retention time
Simmon Verderber model fails

ϕ(Pt) = 5.35eV; ϕ_{offset} (0V)=1.35eV
2 Dead layers of 2nm each; K_{DL}=22:
Acceptors V_{A}: N_{A}=10^{17} cm^{-3};
Donors V_{D}: N_{D}=10^{17} cm^{-3};