Redox-based Resistive Switching Memories – the Mystery of Nanoionic Processes

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Outline

1 Introduction – classification & generic processes
2 Brief survey of the redox-based resistive switching memories
3 VCM systems – the forming process
4 VCM-systems – switching polarity and kinetics
5 Implications on scaling
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Introduction
## Classification of the working principle

### Resistive Switching by Thermal / Chemical / Electronic Mechanisms

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### Material Impact

- Chalcogenide Dominated
- Electrode Dominated

### Switching Polarity

- Unipolar
- Bipolar

### Primary Mechanism

- Thermal Effect
- Redox-Related Chemical Effect
- Electronic Effect
## Classification of the Working Principle

### Resistive Switching by Redox-Based Mechanisms (ReRAM)

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Processes during redox-based switching

Note: these are all conceivable (relevant) processes during forming and switching. The actual processes depend on the type of ReRAM.
Requirements

... to compete with Flash

Endurance: \( > 10^7 \) cycles \( (\text{Flash} \ 10^3 \ ... \ 10^7) \)

Resistance ratio: \( R_{\text{OFF}} / R_{\text{ON}} > 10 \)

Scalability: \( F < 22 \) nm and/or 3-D stacking

Write voltage: approx. 1 ... 5 V \( (\text{Flash} > 5 \) V\)

Read voltage: 0.1 ... 0.5 V

Write speed: < 100 ns \( (\text{Flash} > 10 \mu\text{s}) \)

Retention: \( > 10 \) yrs

Voltage – time dilemma

Kinetics of switching process requires non-linearity of \( > 15 \) orders of magnitude
Link between devices and physics

Criteria of ReRAM

1. Existence of a (compositional) state variable $x$, such that
   \[ I = G(x, V) \cdot V \]

2. Kinetics of change of $x$ controlled by $V$
   \[ \dot{x} = f(x, V) \]

3. Ultrahigh non-linearity of the kinetics
   \[ \dot{x} = x_0 \left( \frac{(V - V_{th})}{V_0} \right)^n \quad \text{with} \quad n >> 1 \]

4. Limits to the range of $x$
   \[ x_{\text{min}} \leq x \leq x_{\text{max}} \]

Memristors as defined by Leon Chua [1971, 1976, 2011]
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Brief survey of the redox-based resistive switching memories

- Interplay of electrochemical and thermochemical effects
- ECM, VCM, TCM

R. Waser, IEDM Tech. Dig. 2008
Operation

**ON-switching:**
Reduction @ cathode
→ Ag filament formation

\[ \text{Ag}^+ + e^- \rightarrow \text{Ag} \]

_M. Faraday (1834)_

**OFF-switching:**
Oxidation @ anode

\[ \text{Ag} \rightarrow \text{Ag}^+ + e^- \]

Electrolyte

* amorphous GeSe\(_{2+x}\)
  and GeS\(_{2+x}\)

* Disordered and amorphous sulfides and oxides

*C. Schindler et al., IEEE T-ED, 54 (2007) 2762*
ECM - Processes during switching

Sketch shows initial stages of the SET process

Comprehensive Review on ECM:
I. Valov, R. Waser, J. Jameson, M. Kozicki., Nanotechnology 22 (2011)
VCM – Valence Change Memories

SrTiO₃: nanocrystalline thin film by sputter deposition

S. Schmelzer et al. (to be published)
VCM - Illustration of the resistive switching

Modification of the barrier by ion transport and redox processes

... using extended filaments as „heating rods“

K. Szot et al.  
& R. Waser, et al.  
*Adv. Mat.* (2009)
VCM - Processes during switching

Sketch shows the SET process
TCM - Thermochemical (Fuse-Antifuse) Memories

Example: lateral Pt/CuO/Pt cell

SET process

- Controlled dielectric breakdown by thermal runaway
  - formation of a conducting filament (fuse formed)

\[
2\text{CuO} \rightarrow \text{Cu}_2\text{O} + \text{O(s)} \\
\text{Cu}_2\text{O} \rightarrow 2\text{Cu} + \text{O(s)}
\]

RESET process

- Thermal dissolution of the filament (fuse blow)
  - disconnected filament

R. Yasuhara, H. Kumigashira, Tagaki, et al., WOE 2008

Differential XAS edge images
Toggle between bipolar and unipolar switching
⇒ demonstrated for TiO2 thin films (D. S. Jeong et al. 2006)
High current compliance ⇒ unipolar fuse/antifuse switching

Temperature profile

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

Thermodiffusion in an extremely high T-gradient

D.S.Jeong et al., 2007
Thermochemical behaviour of transition metal oxides

Temperature dependence of the free formation energy $\Delta G^0$

$\Rightarrow$ redox characteristics: lower valent states more stable at higher T
TCM - Processes during formation and SET

- Electron transport
- Ion transport
- Ad-atom diffusion
- Concentration polarization
- Phase formation
- Space charge formation
- No anodic redox process
- Joule heating
- No cathodic redox process
- Thermo/thermochemical redox process

\[ 2\text{NiO} \rightleftharpoons \text{NiO}_{1-\delta} + \text{NiO}_{1+\delta} \]

Comprehensive Review on TCM:

D. Ielmini, R. Bruchhaus, R. Waser, Phase Transitions 84 (2011)
3

VCM-Systems – the forming process

- phase formation
- forming into the OFF state
  and the ON state
Bipolar resistive switching in transition metal oxides

Example $\text{SrZrO}_3$ (0.2 at% Cr)

Thin film systems
- $\text{SrZrO}_3$, $\text{SrTiO}_3$
- $(\text{Pr,Ca})\text{MnO}_3$
- $\text{TiO}_2$
- etc.

Single crystals
- $\text{SrTiO}_3$
- $\text{TiO}_2$

Characteristics
- Typically forming required
- Bipolar resistive switching by asymmetric cell

Forming – Morphological changes

Evolution of crater structure
- increased defect density
- increased Sr content near surface

“Only formed“ junction

Sr3d +34%
Ti2p -15%

“Sr Droplets upon heating“


Forming – Phase formation

HRTEM study of formed TiO2 films

Identification of Magnelli phases Ti4O7

Processes during formation into the OFF state

- electron transport
- ion transport
- ad-atom diffusion

- concentration polarization!
- phase formation!
- Space charge formation?

- Pt
- SrTiO$_3$
- Ti

- electrons

- anodic redox process, e.g.

\[
\frac{1}{2} O_2 + V_0^{\cdots} + 2e^- \xrightleftharpoons[\text{oxidation}]{\text{O}_0} 
\]

- Joule heating

- thermochemical redox process?

- no cathodic redox process, i.e. ion blocking
Details of the forming process: Initial situation

Metal / n-semiconductor Schottky diode

Band diagram of the fully depleted oxide thin film

Profile of the electrical field
Details of the forming process: electronic process

Metal / n-semiconductor Schottky diode - under forward bias

Band diagram for forward biased cell - electron flow

Profile of the electrical field
Details of the forming process: ionic process

Processes involving ions:
1. Anodic oxidation of $O_2^-$
2. Generation of oxygen vacancies and their drift towards the cathode

$\frac{1}{2}O_2 + 2 e^- \rightarrow O^{2-}$

$O_2$ are released to the gas phase or adsorbed by the grain boundaries of the Pt electrode.

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Details of the forming process: overall process

- generation of oxygen vacancies at the anode
- drift towards the cathode
- formation of a virtual cathode which approaches the anode
Details of the forming process: overall process

- generation of oxygen vacancies at the anode
- drift towards the cathode
- formation of a virtual cathode which approaches the anode

=> termination of the forming process by current compliance (or else)
Details of the forming process: overall process

- generation of oxygen vacancies at the anode
- drift towards the cathode
- formation of a virtual cathode which approaches the anode

=> final situation: OFF state
Forming into the OFF and ON state

C. Nauenheim et al., APL (2010)
Towards forming-free systems

- reduction of switching layer thickness
- ... while keeping an reduced layer as virtual cathode

R. Bruchhaus et al., MRS Proc. 2011

B. Govoreanu et al., IEDM 2011
VCM-Systems – switching polarity and kinetics

- polarity: eight-wise and counter-eight-wise
- origin of the ultra-nonlinear kinetics
Illustration of the resistive switching

Modification of the barrier by push/pull of oxygen vacancies

... using extended filaments as „heating rods“

K. Szot et al.  
& R. Waser, et al.  
*Adv. Mat.* (2009)
Redox-process at dislocations


Tip-induced switching of dislocations in SrTiO$_3$

Observation of two switching polarities

Blue curve: polarity consistent with Interface-switching

Red curve: polarity consistent with conventional VCM switching

Sr$_2$TiO$_4$ (also observed for SrTiO$_3$:Fe)

Observation of two switching polarities


Top electrode peeling & LC-AFM study underneath

Formation crater and halo area around

epi-SrTiO$_3$ (Fe)

Topography
LC-AFM image
Observation of two switching polarities

epi-SrTiO$_3$ (:Fe)


Selective LC-AFM Switching of halo and crater
Switching kinetics of TiO$_2$ cells

Pulse testing

- SET-time < 10 ns
- Limitation: R only before and after
- When does the cell actually switch?

Ultrafast switching kinetics of TiO$_2$ cells

Initial system developed for ultrafast pulse testing of unipolar PCM cells

G. Bruns et al., APL 2009

Extended into bipolar operation

- 2 ns rise time
- 200 ps resolution
- Optimized to suppress reflections

C. Hermes et al., EDL 2011
Modeling: Switching kinetics of VCM cells

3-D FEM simulation

Conductivity = f(T) - exper. data

3-D FEM simulation of the thermal, electrical, and ionic transport processes

S. Menzel et al. (Adv. Funct. Mat. 2011)
3-D FEM simulation of the thermal, electrical, and ionic transport processes

- Joule heating of the conducting filament
- Thermally activated oxygen vacancy drift
- Concentration change affects the electronic conductivity (based on generic lattice disorder model of metal oxides)

Experimental data

Pulse width vs. SET voltage experiments

- Perfect fit to simulation
- Non-linearity of > 9 orders of magnitude

S. Menzel et al. (Adv. Funct. Mat. 2011)
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Implications on Scaling
Scaling of integrated cells

B. Govoreanu et al., IEDM 2011
Scaling towards atomic resolution

\[
\begin{align*}
I &\sim 1.2 \text{ nA} \\
I &\sim 0.009 \text{nA}
\end{align*}
\]

\[N. \text{Szot et al., Nature Mat. (2006)}\]

\[Aono et al, Nature (2005)\]

\[\text{ECM cells}\]

\[\text{VCM cells}\]

\[1 \text{nm}\]
Scaling towards atomic resolution

Barrier lowering

Lateral displacement of atoms

Q: How many atoms must be moved?

-> Theory:
Displacement of 2 atoms sufficient for ROFF/RON = 470 and barrier > 1.5 eV

ReRAM cells in real arrays

Parasitics of empty arrays

ReRAM cells in real arrays

Constraints by thermal assistance of the switching process

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Ultradense and 3-D stackable Architecture Concepts
Advantages
• simple structure
• small area ($4 F^2$)
• easy to manufacture

• high scalability
• suited for two terminal devices
Passive Arrays – Sneak Path Problem

- $\Delta I = I_{\text{sense},2} - I_{\text{sense},1} \rightarrow \Delta V$
- several elements in LRS
  $\rightarrow$ Reading is disturbed

- $\Delta V$ small even for small arrays
- pattern dependencies
  – circuitry difficult to design
  – static power consumption high
  $\rightarrow$ Only small arrays can be built

Alternative:
$\rightarrow$ Sneak paths must be avoided

Conventional attempts:
Non-linear (Z-diode type) elements in series
Problems:
$\rightarrow$ Read dynamics reduced
$\rightarrow$ High current density
Complementary resistive switch (CRS)
- two antiserial memristive elements

CRS in a Passive Array
- high cell resistance
- not pattern dependent
- low static power losses

Complementary Resistive Switch (CRS)

Write operation:

- write 1: $V < V_{th,4}$
- write 0: $V > V_{th,2}$

• 1 and 0: high resistive

E. Linn, et al.  
Complementary Resistive Switch (CRS)

Read operation:

\[ V_{th,1} < V < V_{th,2} \]

- high current: read 1
- low current: read 0

\[ \rightarrow \text{Easy to distinguish} \]
\[ \text{(but: destructive Read-out like in FeRAM !)} \]

<table>
<thead>
<tr>
<th>CRS state</th>
<th>element A</th>
<th>element B</th>
<th>resistance CRS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>HRS</td>
<td>LRS</td>
<td>( \approx \text{HRS} )</td>
</tr>
<tr>
<td>1</td>
<td>LRS</td>
<td>HRS</td>
<td>( \approx \text{HRS} )</td>
</tr>
<tr>
<td>ON</td>
<td>LRS</td>
<td>LRS</td>
<td>LRS+LRS</td>
</tr>
<tr>
<td>OFF</td>
<td>HRS</td>
<td>HRS</td>
<td>( \gg \text{HRS} )</td>
</tr>
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E. Linn, et al.  
Concept: different cell areas within the CRS cell & capacitive read-out

Proof: Pt/TiO2(8nm)/Cu/TiO2(8nm)/Pt cells

S. Tappertzhofen, et al., Nanotechnology (2011)
7 Conclusions
Challenges

- Design rules not yet fully known
  ... to guide search in the material´s „treasure map“

- Long-term reliability
  ... and overcoming the voltage-time dilemma

- Defect engineering
  ... just at it´s very beginning

- Highly scaled interconnect lines
  ... and reliable electrode contacts

Prospects

- Technologically compatible to CMOS interface

- Ultimately high scaling potential
  .... of redox-based resistive switching concepts

- Functions beyond pure memory
  ... from FPGA type logic to neural functions to cognitive computing
Frontiers in Electronic Materials: Correlation Effects and Memristive Phenomena

Aachen, Germany
Eurogress Conference Centre

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http://www.nature.com/natureconferences/fem2012
Thank You!