RRAM-An Emerging Non-Volatile Memory Technology

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Outline

- An overview of Non-volatile memory
- RRAM technology: Opportunities and Challenges
- RRAM research in IMECAS
- Summary
Flash Memory

Concepts proposed by D. Kahng and S. M. Sze, Bell Lab, 1967


- Uses Fowler-Nordheim tunneling to erase the memory
- Uses CHE or FN to program the memory
- The NVM bit information is represented by the change in \( I_d-V_g \) curve of the read-transistor connected to the floating gate

Dominated the NVM in the last two decades
Flash Scaling Challenges

Physical limitations exist!
— leakage current
— High voltage operations
— Charge storage requirements of the dielectrics and reliability issues
— Slow writing speed

<table>
<thead>
<tr>
<th>Year</th>
<th>Node</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999</td>
<td>180 nm</td>
</tr>
<tr>
<td>2001</td>
<td>130 nm</td>
</tr>
<tr>
<td>2003</td>
<td>90 nm</td>
</tr>
<tr>
<td>2007</td>
<td>65 nm</td>
</tr>
<tr>
<td>2009</td>
<td>45 nm</td>
</tr>
<tr>
<td>2012</td>
<td>25 nm</td>
</tr>
<tr>
<td>2015</td>
<td>16 nm?</td>
</tr>
</tbody>
</table>

It is very hard for conventional Flash memory to go through 16 nm node!
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What is RRAM?

Advantages of RRAM:

- Simple device structure (Metal/Insulator/Metal)
- Good compatibility with CMOS process
- Easy scaling down to 8 nm
- Large on/off ratio ($10^3$~$10^6$)
- Fast operating speed (~ns)
- Good endurance (>10$^6$)
- Good retention (>10 years)

Materials for RRAM

<table>
<thead>
<tr>
<th>Class</th>
<th>Typical Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMO (Transition Metal Oxide)</td>
<td>$\text{Cu}_{x}\text{O}, \text{TiO}_x, \text{ZrO}_x, \text{NiO}_x, \text{VO}_x, \text{CeO}_x, \text{AlO}_x, \text{HfO}_x, \text{MnO}_x$</td>
</tr>
<tr>
<td>Metal doped perovskite</td>
<td>PCMO, Cr-SrTiO$_3$, Cr-SrZrO$_3$,……</td>
</tr>
<tr>
<td>Chalcogenide</td>
<td>GeSbTe……</td>
</tr>
<tr>
<td>PMC (programmable metallization cell)</td>
<td>$\text{Cu-SiO}_2$, $\text{Cu-WO}_x\text{TaO}_x$, $\text{Cu}_2\text{S}, \text{GeTe}$,……</td>
</tr>
</tbody>
</table>
RRAM is not suitable for working memory, but quite competitive for embedded and stand-alone NVM application.
## Challenges for RRAM

### 1. Switching mechanism:

<table>
<thead>
<tr>
<th>Electronics effect based memory</th>
<th>Fuse/anti-fuse memory</th>
<th>Cation redox based memory</th>
<th>Anion redox based memory</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Electronics effect based memory" /></td>
<td><img src="image2" alt="Fuse/anti-fuse memory" /></td>
<td><img src="image3" alt="Cation redox based memory" /></td>
<td><img src="image4" alt="Anion redox based memory" /></td>
</tr>
<tr>
<td><strong>Excellent uniformity</strong></td>
<td><strong>Unipolar switching</strong></td>
<td><strong>High speed</strong></td>
<td><strong>High speed</strong></td>
</tr>
<tr>
<td><strong>Multilevel</strong></td>
<td><strong>Easy to 1D1R</strong></td>
<td><strong>Lower Power</strong></td>
<td><strong>Lower Power</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Good retention</strong></td>
<td><strong>Excellent scalability</strong></td>
<td><strong>Excellent scalability</strong></td>
</tr>
<tr>
<td><strong>Poor scalability</strong></td>
<td><strong>High power</strong></td>
<td><strong>Poor retention</strong></td>
<td><strong>Poor retention</strong></td>
</tr>
<tr>
<td><strong>Poor retention</strong></td>
<td><strong>Electroforming</strong></td>
<td><strong>Poor uniformity</strong></td>
<td><strong>Poor uniformity</strong></td>
</tr>
</tbody>
</table>
Challenges for RRAM

2. Which RRAM materials are worthy manufacturing? Contamination free, low thermal budget, acceptable performance,......
Challenges for RRAM

3. Selector challenge for 3D integration:

- Reduce $I_{\text{reset}}$—less diode current required
- Increase current density of Diode, rectifying ratio of Diode and decrease fabrication temperature.

D. Kau, IEDM, 2009

![Diagram showing a trade-off between Reduce RRAM Reset current <1 uA and Increase current density & rectifying ratio.]

**Trade off**
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RRAM research in IMECAS

- Switching Mechanism Study
- Device performance improvement
- Solution for 3D Integration
- Statistics Modeling Work
- Integration
Mechanism of Resistive Switching

The unclear switching mechanism hinders rapid development for RRAM

The general accepted mechanism of RRAM:
Formation and rupture of localized conductive filaments (CF).

R. Waser, Nature. Mat. 2007
Solid-electrolyte-based RRAM

CF formation process:

i) anodic metal atoms (M) oxidize metal ions (M$^{z-}$) according to the reaction (M $\rightarrow$ M$^{z-}$ + ze$^{-}$)

ii) the M$^{z-}$ cations migrate toward the cathode under the high electric field;

iii) M$^{z-}$ deoxidize back to M and electrodeposits on the surface of the inert electrode according to the reversed reaction (M$^{z-}$ + ze$^{-}$ $\rightarrow$ M)

Solid electrolyte materials: AgS, CuS, AgGeSe, SiO$_2$, Ta$_2$O$_5$, ZrO$_2$, HfO$_2$, ZnO, a-Si, …

Formation and Rupture Conductive Filament

- What’s the evident for this mechanism?
- Composition of CF?
- How many CF?
- Dynamic process of CF formation and rupture?
- Do CF growth and dissolution be controlled?

How to capture the dynamic process of CF formation and rupture is a very tough topic to study because of the difficulties in sample preparing.
Conductive Filaments Mechanism

- The resistive switching phenomena are dominated by conductive filaments mechanism
  - The current slope is close to 1 in ON state.
  - $I_{\text{Reset}}$ increases with increasing $I_{\text{Comp}}$ in Set process.
  - The resistance of ON state is insensitive to the cell sizes.

How to confirm the nature of filaments is a trouble to RRAM researcher.

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In the LRS, thermal coefficient is $0.00298/K$ @ $293K$ ($5 \times 5 \mu m$), $0.00249/K$ @ $293K$ ($10 \times 10 \mu m$) and $0.00239/K$ @ $293$ ($20 \times 20 \mu m$)

Thermal coefficient of Cu nanowire (>15nm) is $0.0025/K$ @ $293K$

Conduction in LRS arises from copper metal!

How many of CF?

Observed a stair-like I-V by ultra low sweeping speed, demonstrated the existence of multi filaments.

The simulation of electric field distribution of CFs under different growth stages uses the MATLAB PDE-tool, (a) pre-connection (b) connect establishment and (c) post-connection. Simulating result indicate that multiple cylinder-like CFs will be formed in the Cu-doped ZrO$_2$ film.
Multiple Filaments Mechanism

The stepwise switching behavior can be explained by multiple parallel filaments are successively connected between the bottom and top electrodes during set process. The resistance steps in on-state follow the inverse relationship of forming sequence of these filaments, further verifying the multiple filaments mechanisms.

Fabrication technique for ReRAM TEM specimen
Dynamic process of CF formation and rupture

Qi Liu, et al., Advanced materials, accepted
Growth of the multiple conductive filament

Under voltage stress, the dynamiitic growth of the conductive filament were observed in the above movie. As can be seen from the video, there are two conductive filaments were formed from the Cu to the Pt electrodes through the ZrO₂ layer.
In oxide based electrolyte material, the metal bridge is found grown from the anode, rather than the cathode, which is opposite to the conventional PMC theory.
Dynamic process of CF Rupture

The rupture process, from the cathode, also opposite to the conventional theory.

(Qi Liu, et al., Advanced Materials accepted)
CF growth by inserting nano-crystal

- Ion + Atom + + +

Cu(Ag) TE

ZrO$_2$ oxidized

Reduced Metal NC

Pt BE

- Enhancing and converging the electrical field by metal NC
- Accelerating metal ions velocity
- Controlling filament growth location by metal NC

i) Anodic metal atoms (M) oxidize metal ions (M$^{z-}$) according to the reaction (M → M$^{z-}$ + ze$^-$)

ii) The M$^{z-}$ cations migrate toward the cathode under the high electric field, more M$^{z-}$ gathered around NC;

iii) M$^{z-}$ deoxidize back to M and electrodeposits on the surface of the inert electrode according to the reversed reaction (M$^{z-}$ + ze$^-$ → M)

Qi Liu, et al., EDL 31(11) 1299
The maximum intensity of $E$ at the NC tip increases exponentially with the NC size.
The intensity of $E$ rapidly decays outside the column region above the NC location.

Qi Liu, et al., EDL 31(11) 1299
TE/ZrO₂/Cu NC/Pt

- clear Si wafer
- thermal SiO₂ layer
- deposit BE electrode materials
- deposit Cu thin film (3nm)
- deposit ZrO₂ film (40 nm)
- rapid thermal annealing (600°C, 5s, N₂)
- defining TE electrode shape
- deposit TE electrode materials
- lift-off to forming TE electrode
- electrical test

Qi Liu, et al., EDL 31(11) 1299
The nano-bridge region is directly connected to a protrusion of the Pt BE, and the protrusion is a Cu NC based on elements analysis by EDS!

Qi Liu, et al., ACS Nano. 4, 6162 (2010)
EDS analysis

i) a→b corresponds to the Ag electrode region;
ii) b→c corresponds to the CF electrode region;
iii) c→d corresponds to the Cu NC region.
Element mapping

The component of nano-bridge in the Ag/ZrO$_2$/Cu NC/Pt device is mainly Ag elements!

Qi Liu, et al., ACS Nano. 4, 6162 (2010)
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Temperature-dependent switching characteristics reveals that microscopic nature of the metallic conductive is Cu element in Cu/BTMO:Cu/Pt based RRAM.

Multiple resistance steps in Cu/BTMO:Cu/Pt device was observed, it is due to successively established parallel filaments between the bottom and top electrodes during Set process.

We have indentified the metallic nature of CF in Cu/ZrOx/Pt device and observed the existence of multi-CFs Oxide-Electrolyte-based ReRAM.

Adding a metal NC layer, CFs grow easily along the direction of metal NC, which reduces the randomness of the CF formation and rupture processes.
Thanks for your attention!