Memresistive switching in Ag$_2$S solid electrolyte

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Nanophysics seminar

Classification

- e\textsuperscript{-} injection into an Ag\textsubscript{2}S crystal: reduction of cations, precipitation on the surface
- SEM: controlling the position and irradiation time of the e\textsuperscript{-} beam: Ag nanodots can be formed in a patterned structure
- STM mode \textsuperscript{2} or crossbar structure

\textsuperscript{2}K. Terabe et al., JAP, 91, 12 (2002)
Gap-type atomic switch - STM mode

\[
\frac{dl}{dt} = A \exp(-D \cdot It)
\]

\(\frac{dl}{dt}\) does not depend on bias

A, D : coefficients

It: tunnel current

Images (a) and (b) show the STM mode of Gap-type atomic switch. The change in tip height is plotted in (c) with different values of biasing voltage (1: \(V_S = -2.0\, \text{V}\), \(I_t = 0.05\, \text{nA}\); 2: \(V_S = -2.0\, \text{V}\), \(I_t = 1.35\, \text{nA}\); 3: \(V_S = +2.0\, \text{V}\), \(I_t = 0.05\, \text{nA}\); 4: \(V_S = +2.0\, \text{V}\), \(I_t = 0.35\, \text{nA}\)).
- $10^5$ switches
- switching time: $R$ decreases from 1 MΩ to 12.9 kΩ
Crossbar structure - switching time

(a) $t_{sw} \propto e^{\beta V_{sw}}$
- $\beta_1 = 67.7 \text{ V}^{-1}$
- $\beta_2 = 32.9 \text{ V}^{-1}$

(b) $t_{sw} \propto e^{\beta V_{sw}}$
- $\beta_1 = 54 \text{ V}^{-1}$
- $\beta_2 = 25 \text{ V}^{-1}$

(c) $E_a = 0.508 \text{ eV}$

(d) $E_a = 1.26 \text{ eV}$
Gapless-type atomic switch

- conductive path is made in an ionic conducting material
- forming process
- electric field-driven activated hopping
- min. switching time: 5 ns
- $\text{Ag}_2\text{S}$: on/off ratio: $10^5$, switching speed: 1 ms
Shortest switching time

Cu bridge in an insulator $^3$

- 5 ns switching time
- series transistor: current limiter during the set
- symmetric, unipolar
- long reset time, large reset current

redox reactions: Ti-doped NiO $^4$

Table 1. Typical parameters and key features.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEOL</td>
<td>180-nm CMOS</td>
</tr>
<tr>
<td>Active cell area</td>
<td>40 nm$^2$</td>
</tr>
<tr>
<td>Set pulse width</td>
<td>5 ns</td>
</tr>
<tr>
<td>Set current</td>
<td>110 $\mu$A</td>
</tr>
<tr>
<td>Set voltage</td>
<td>+3 V</td>
</tr>
<tr>
<td>Reset pulse width</td>
<td>1 ns</td>
</tr>
<tr>
<td>Reset current</td>
<td>125 $\mu$A</td>
</tr>
<tr>
<td>Reset voltage</td>
<td>-1.7 V</td>
</tr>
<tr>
<td>Resistance read voltage</td>
<td>+0.1 V</td>
</tr>
<tr>
<td>Endurance</td>
<td>$10^7$ cycles</td>
</tr>
</tbody>
</table>

Towards a quantitative description of solid electrolyte conductance switches\textsuperscript{5}

Theory: Hebb and Wagner model

\[-eV = \varepsilon''_F - \varepsilon'_F = \mu''_e - \mu'_e\] (1)

': Ag electrode, ': Pt electrode

\[j_e = \frac{\sigma_e}{e} \nabla \mu_e\] (2)

\[j_{Ag^+} = -\frac{\sigma_{Ag^+}}{e} \nabla \mu_{Ag^+}\] (3)

local thermodynamic equilibrium:

\[\mu_{Ag} = \mu_{Ag^+} + \mu_e\] (4)

\[-eV = (\mu''_{Ag} - \mu'_Ag) - (\mu''_{Ag^+} - \mu'_Ag^+)\] (5)

\(t >> 0:\)

\[\nabla \mu_{Ag^+} = 0, j_{Ag^+} = 0\] (6)

\[\nabla \mu_e = \nabla \mu_{Ag}, j_{total} = j_e\] (7)

\textsuperscript{5}Morales-Masis, Ruitenbeek et al., Nanoscale, 2, 2275 (2010)
Towards a quantitative description of solid electrolyte conductance switches

\[ e\mathbf{j}_{total}(\mathbf{r}) \cdot d\mathbf{r} = \sigma_e d\mu_{Ag} \]  
(8)

\[ e \int_{r'}^{r''} \mathbf{j}_{total}(\mathbf{r}) \cdot d\mathbf{r} = -\frac{e}{K} I \]  
(9)

\[ \sigma_e = \sigma_0 e^{(eV/kT)} \]

\[ I(V) = K\sigma_0 \frac{k_B T}{e} \left( e^{(eV/k_B T)} - 1 \right) \]  
(10)

in AFM geometry: \( K = 2\pi a \)
Towards a quantitative description of solid electrolyte conductance switches

- deposition of Ag$_2$S: sputtering Ag in Ar/H$_2$S plasma on top of a Ag film
- Ag$_2$S layer thickness: approx. 200 nm, with 30 nm roughness, 5x5 mm$^2$
- Ag: 100 nm, 10x10 mm$^2$
- room temperature measurements
Towards a quantitative description of solid electrolyte conductance switches

tip contact radius: $a = K/(2\pi) = 12\text{nm}$

Simulation:

$$\delta = n - p = 2K^{1/2}i \sinh\left(\frac{e(V_0 - V(d))}{kT}\right)$$

- supersaturation
- nucleation within the silver sulfide
the tip is not in contact with the Ag$_2$S film $\Rightarrow$ gap-type measurement

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Bulk and surface nucleation processes in Ag$_2$S conductance switches

the feedback was too slow ⇒ gapless-type measurement

sample biased and current measured

two processes: nucleation and cluster formation
Bulk and surface nucleation processes in Ag$_2$S conductance switches

$T=240$K

100 s between the forming and the topography scan $\Rightarrow$ cluster shrinks back to the Ag$_2$S
Quantized conductance steps in Ag$_2$S$^7$

$^7$Wanegaar, Ruitenbeek et al., JAP, 111, 014302 (2012)
Quantized conductance steps in Ag$_2$S
W tip grounded, Ag electrode biased

Sample preparation:
- d=0.5 mm Ag wire and S powder annealed in vacuum
- anneal: 200°C, 30 min
- sulfidized Ag wire annealed in argon (200°C, 30 min)
- Ag₂S scratched with a clean Ag wire, small pieces were transferred
- sharp W tip on a piezotube

scale bar: a) 20 nm, b)-c) 50 nm

Xu et al., ACS Nano, 4, 5 (2010)
Real-Time In Situ HRTEM-Resolved Resistance Switching of Ag2S Nanoscale Ionic Conductor

Initial:
- Acanthite

Initial to ON:
- Acanthite → Argentite
- Ag⁺ → Ag

ON:
- Argentite

ON to OFF:
- Acanthite ↔ Argentite
- Ag⁺ ↔ Ag

OFF:
- Acanthite

OFF to ON:
- Acanthite → Argentite
- Ag⁺ → Ag

↔ Phase transition and chemical reaction
« » movement of ions
Applications - Photo sensing

(a) Photoconductive molecule

(b) $V = 5 \text{ V}$
- No light illumination
- Light illumination

(c) Bridging Time (s)
- 5 V Light
- 2 V Light

Gap Width (nm)

Current (nA)

Time ($10^3 \text{ s}$)
Applications - Synaptic operations

- short-term plasticity (STP)
- long-term potentiation (LTP)

2. K. Terabe et al., JAP, **91**, 12 (2002)


6. Wanegaar, Ruitenbeek et al., JAP, **111**, 014302 (2012)


8. Xu et al., ACS Nano, **4**, 5 (2010)