

Bipolar resistive switching in oxides for memory applications

resistance change effect after suitable electrical stimulation

- ◆ Phase Change RAM (PCRAM) -- resistance difference between the amorphous and the crystalline state, ex.: GeSbTe
- ◆ Conductive Bridge RAM (CBRAM), Electrochemical Metallization Memory (ECM) or Programmable Metallization Cells (PCM) -- the electrochemical formation and rupture of very thin metal filaments of Ag or Cu in an ion-conducting material, ex.: GeSe or GeS
- ◆ Resistance change Random Access Memory (RRAM) -- drift of anions, typically oxygen ions (often the oxygen vacancy motion), in transition metal oxides and a subsequent valence change in the cation sublattice. We name this class Valence Change Memories (VCM).

resistance switching in MIM devices

Hickmott (1962)

-- hysteretic resistance change in Al/Al₂O₃/Al MIM structures after application of voltage pulses

Gibbons JF, Beadle WE (1964) -- NiO

Simmons JG, Verderber RR (1967) -- SiO

- ◆ mainly on relatively thick films
- ◆ high voltage is needed.
- ◆ Mostly unipolar

Unipolar and bipolar modes

SET (forming process) -- high resistive "OFF" state → low resistive "ON" state
 RESET -- ON state back to the OFF state
 a compliance unit of the measurement unit to avoid damage to the sample
 $V_{set} > V_{reset}$ and $I_{reset} > I_{set}$

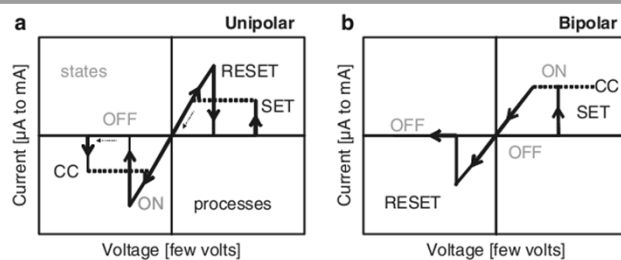


Fig. 4.1 Comparison of unipolar (a) and bipolar (b) switching characteristics. For the bipolar switching SET and RESET processes occur at different polarity. The states ON and OFF received after the switching processes SET and RESET are indicated in gray. CC is a current compliance used to limit the current preventing damage to the memory element

Bipolar switching

- ◆ the first report of bipolar switching:
Hiatt and Hickmott (1965)
bistable switching of Nb_2O_5 with Nb and Bi electrodes

In MIM structure must include some asymmetry for the bipolar switching characteristics.

The origin of asymmetry:

- ◆ different electrode materials
- ◆ a graded composition of the isolator
- ◆ voltage polarity during the initial electroforming step

memory elements in thin film form

- ◆ In single crystals, the progress of the chemically reduced region can be directly observed and it may take several hours at room temperature to form the conducting filament.
- ◆ In thin films it will occur on a much shorter timescale and voltages in the range of 1–5 V may be sufficient.

In the late 1990s
compatibility and integration with CMOS processing
multiple levels of resistance states → multibit memory devices

Theory for the resistance change

In the transition metal oxides , oxygen vacancies frequently have a higher mobility than the cations.



Under bias voltage oxygen vacancies as a positively charged species are attracted by the cathode.



Most of the electrodes are not permeable for oxygen



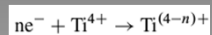
oxygen-deficient region is formed in the vicinity of the cathode.



As an accommodation process to compensate for the oxygen deficiency electrons emitted from the cathode get trapped.

Example: TiO₂

results in a reduction of the Ti-ion



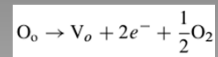
for Ti-oxide typically for $n > 1.5$ in $TiO_{2-2/n}$

reduced valence state changes the oxide into a metallically conducting phase

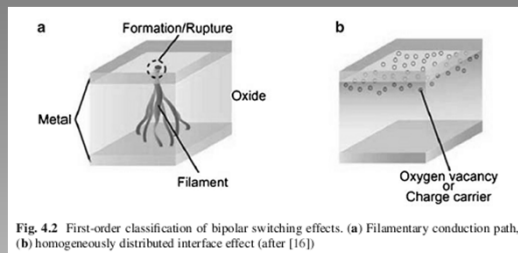


expands into the bulk of the material and forms a “virtual cathode”, which moves toward the anode

At the anode an oxidation reaction is observed,



which may result in the evolution of oxygen or the oxidation of the electrode material.



The geometrical location of the material property change responsible for the switching event can serve as a first-order classification of the bipolar switching effects.

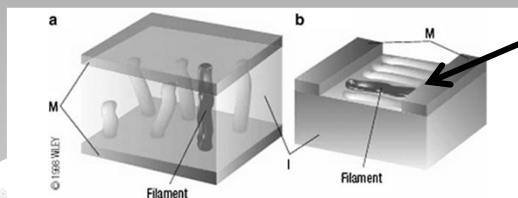


Fig. 4.3 Schematic image of the filamentary conduction in MIM structures. The red-colored filament indicates the lowest resistance path responsible for the ON state resistance. (a) Vertical arrangement between two metal electrodes M (b) horizontal arrangement between two metal electrodes M (after [16])

Can be observed by an OM