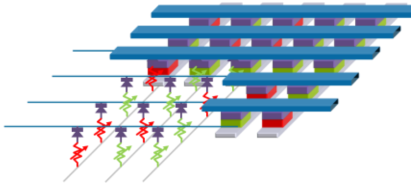
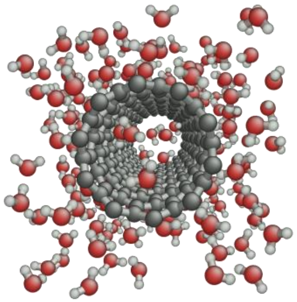
NON-VOLATILE MEMORY DEVICES: FROM SILICON TO ORGANIC MATERIALS





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Lecture for the course «Tecnologie e dispositivi elettronici avanzati»

November 10th , 2015

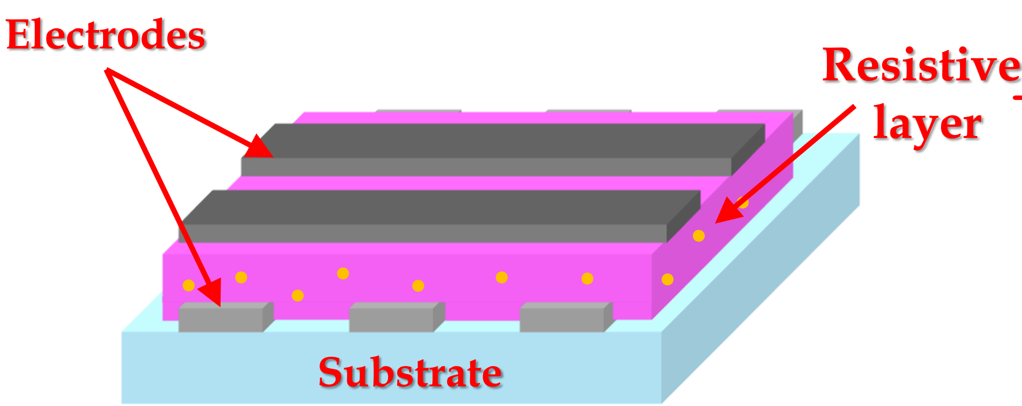
Outline

- Organic Resistor-type memories
  - ➢ Working principle
  - ➢ Electrical characteristics
  - ➢ Basic parameters
  - ➢ Conduction mechanisms:
    - ✓ Filamentary conduction
    - ✓ Space charge and traps
    - ✓ Charge transfer
    - ✓ Conformational change
    - ✓ Ion conduction
  - ➢ Progress in organic resistive memories
  - ➢ Memory performance enhancement
  - ➢ Architectural concepts for advanced memory devices
  - ➢ Developmental status

Organic Resistor-type memories

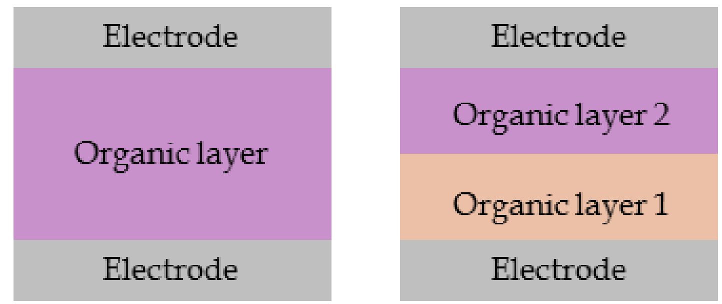
The most promising class of organic two-terminal memories is the **resistive random access memory** (**RRAM**), whose resistance can be (reversibly) switched between low and high states by appropriate voltage pulses

General structure

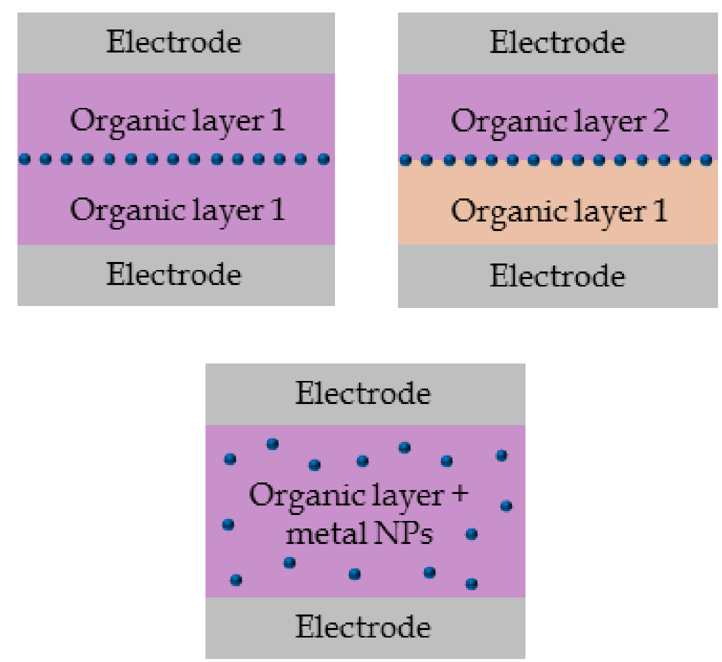


Two terminal elements, consisting of a cross-point array of top and bottom electrodes, separated by a resistive material. Each area where the top and the bottom electrodes cross is a memory cell

Without metal nanoparticles (NPs)

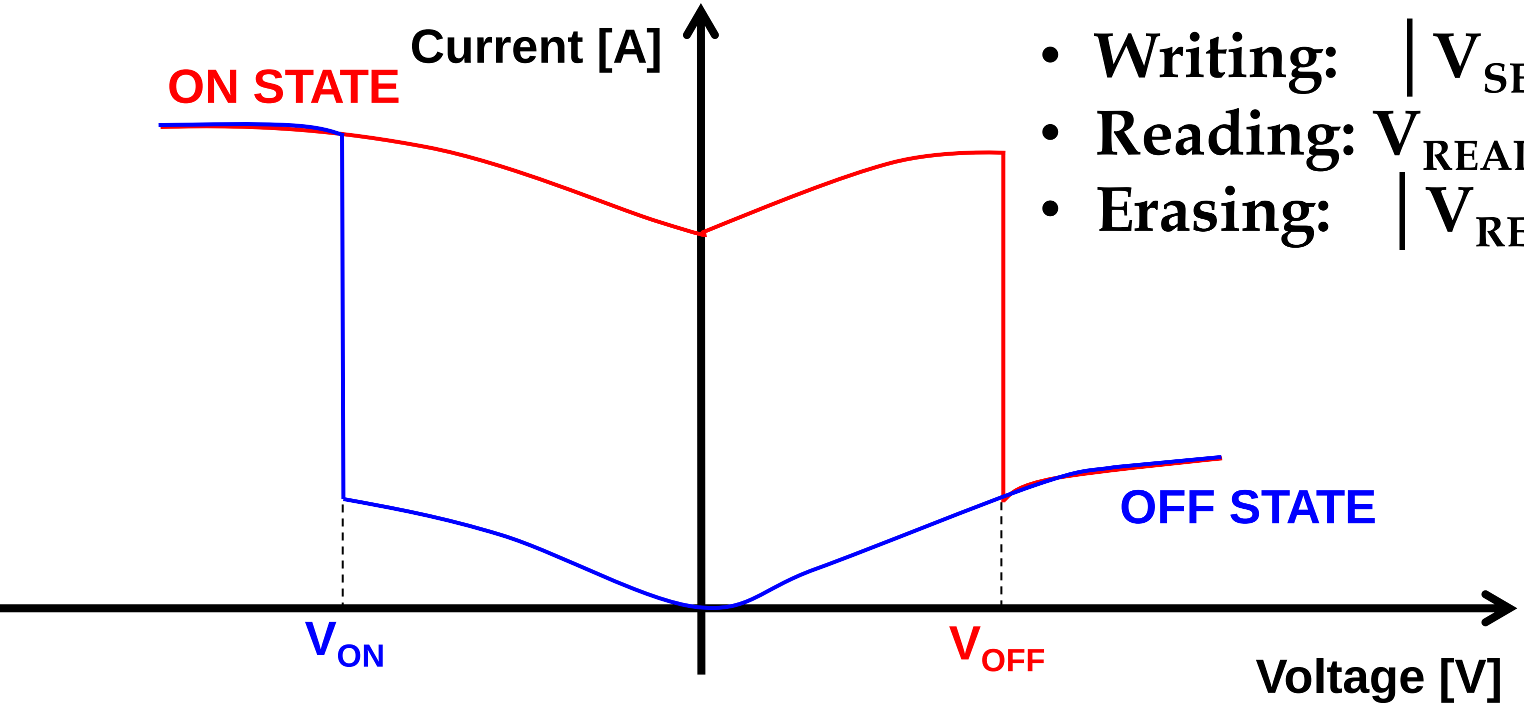


With metal nanoparticles (NPs)



Organic RRAM working principle

Resistive switching

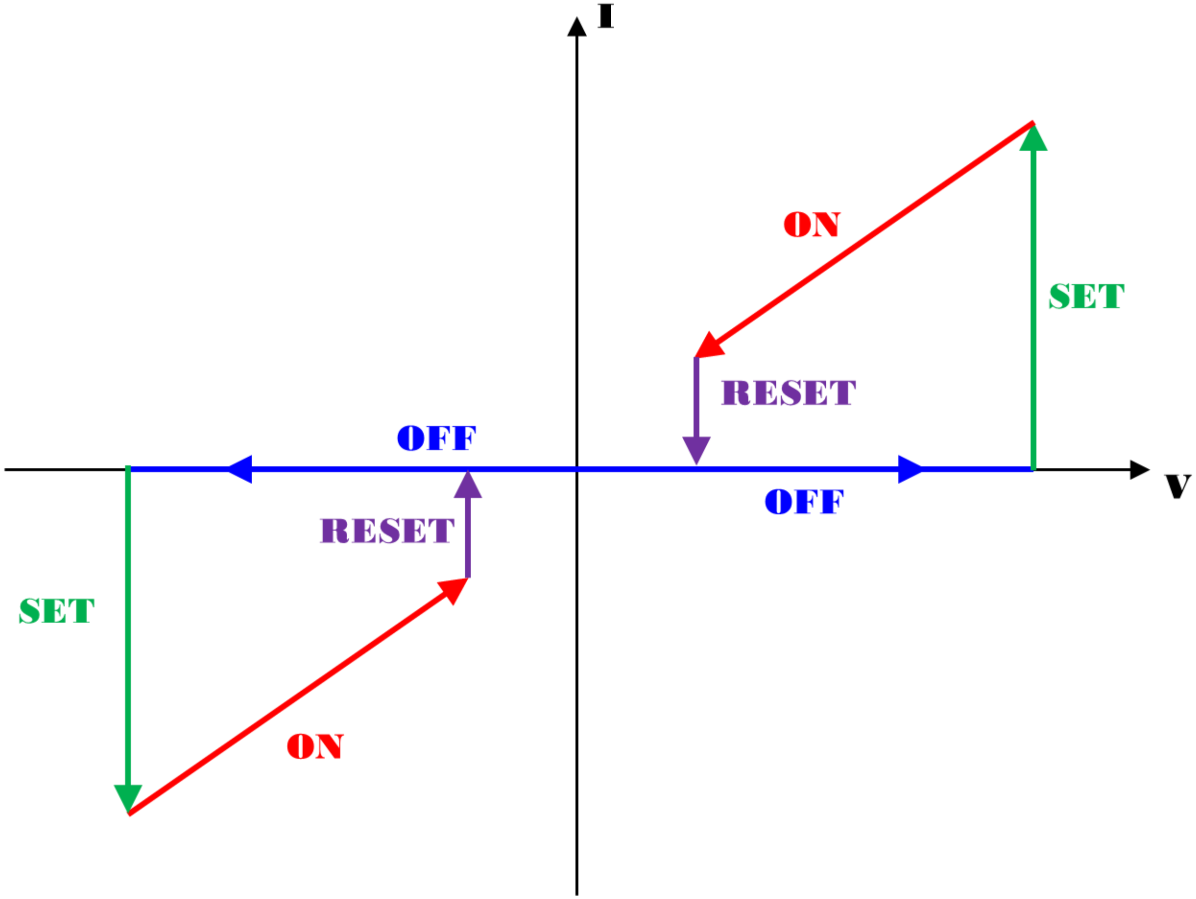


- **Writing:** $|V_{SET}| \geq |V_{ON}|$
- **Reading:** $V_{READ} \sim 0$
- **Erasing:** $|V_{RESET}| \geq |V_{OFF}|$

By applying an appropriate voltage, the resistance of the memory can be reversibly switched between a high resistance state (HRS, or OFF state) and a low-resistance state (LRS, or ON state).

Organic RRAM: electrical characteristics

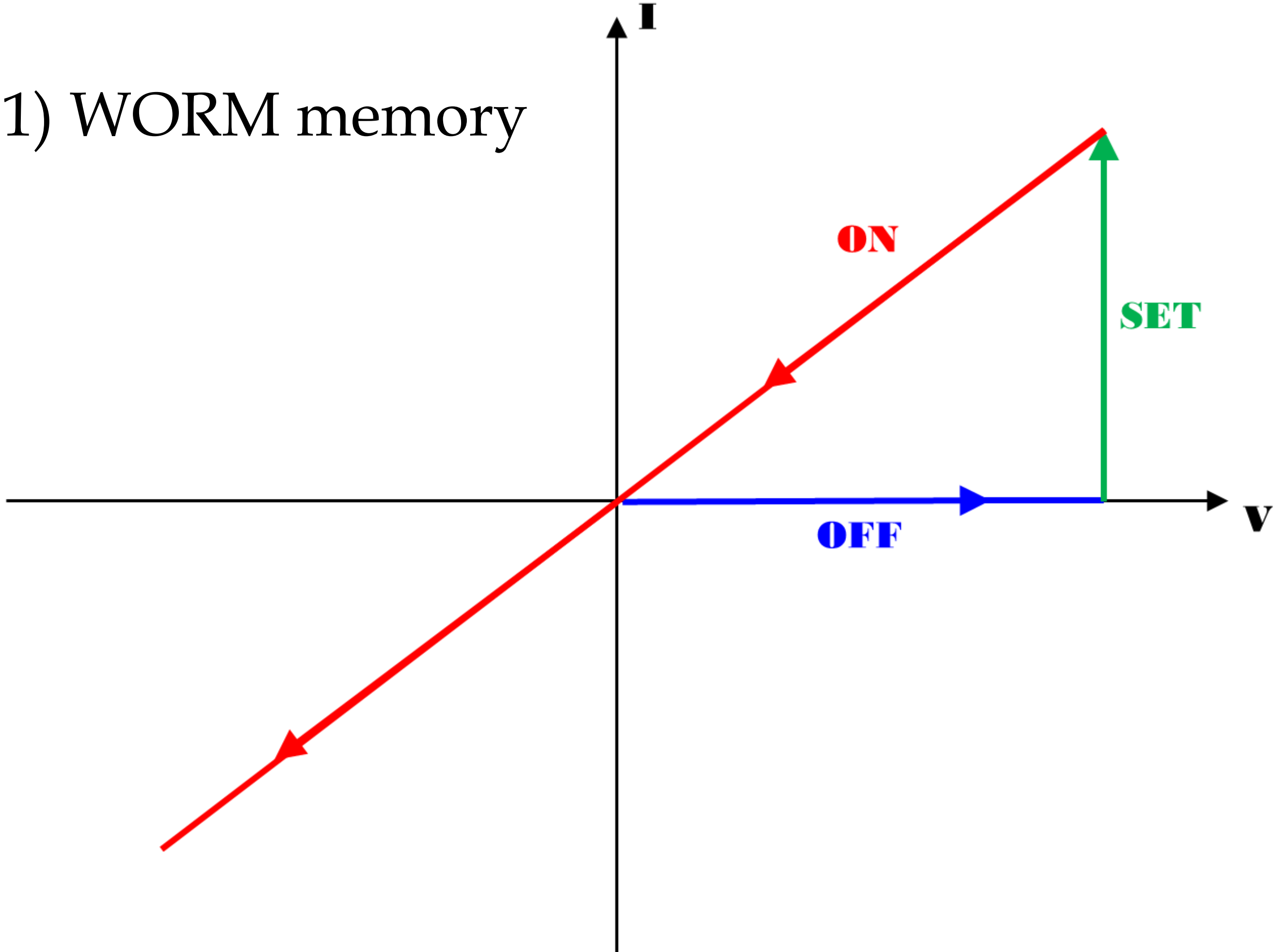
Typical I-V curve of a **volatile** RRAM



Organic RRAM: electrical characteristics

Typical I-V curves of **non-volatile** RRAMs

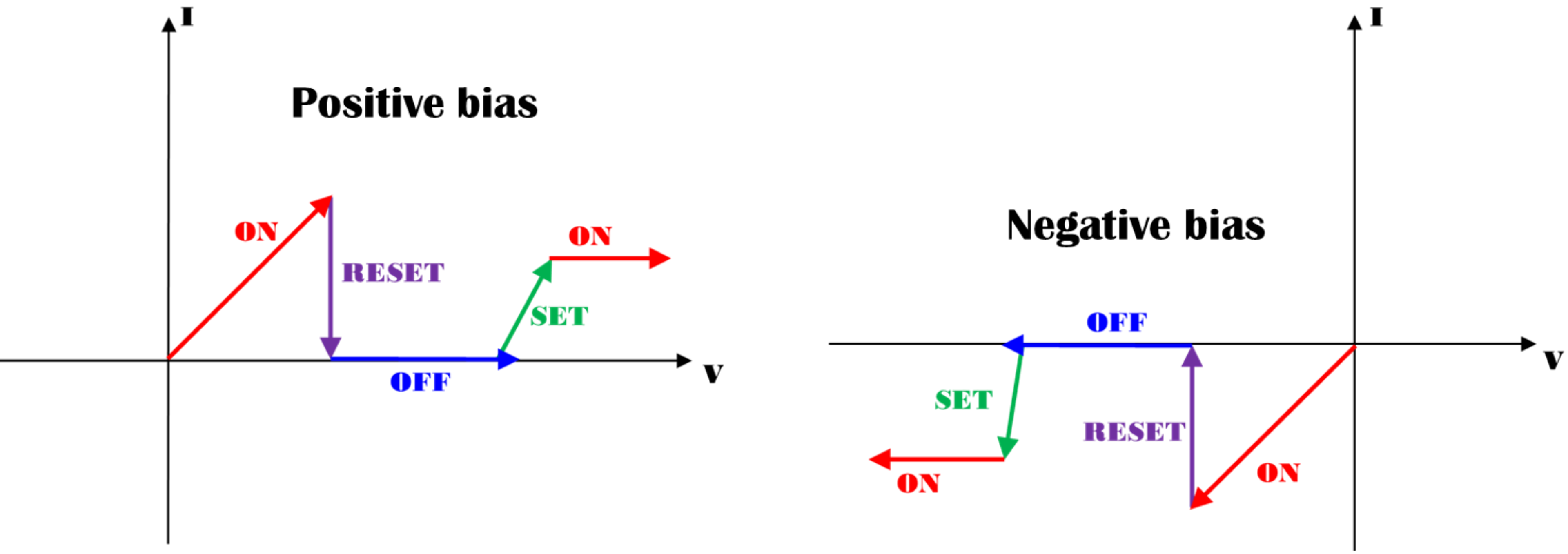
1) WORM memory



Organic RRAM: electrical characteristics

Typical I-V curves of **non-volatile** RRAMs

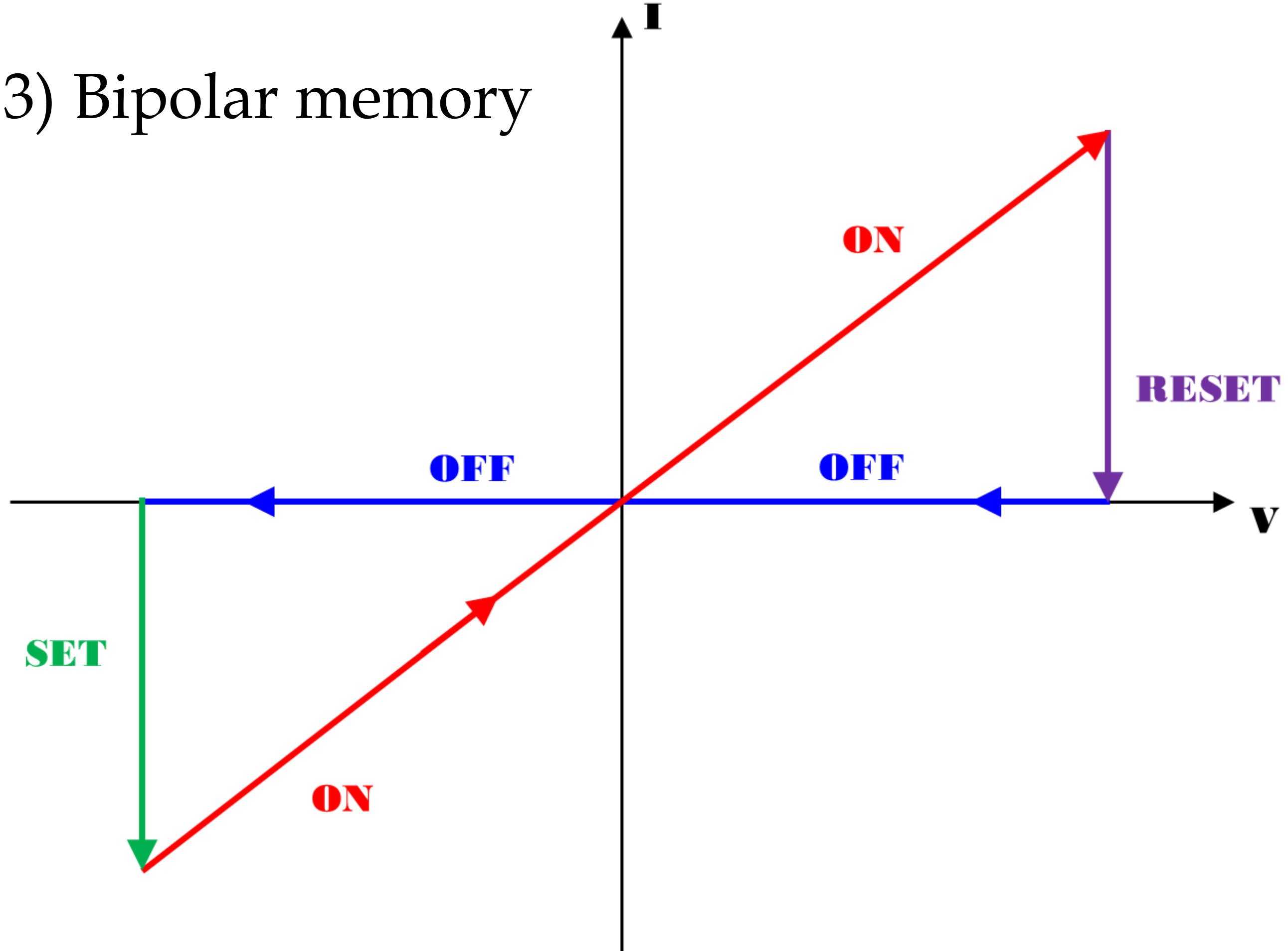
2) Unipolar memory



Organic RRAM: electrical characteristics

Typical I-V curves of **non-volatile** RRAMs

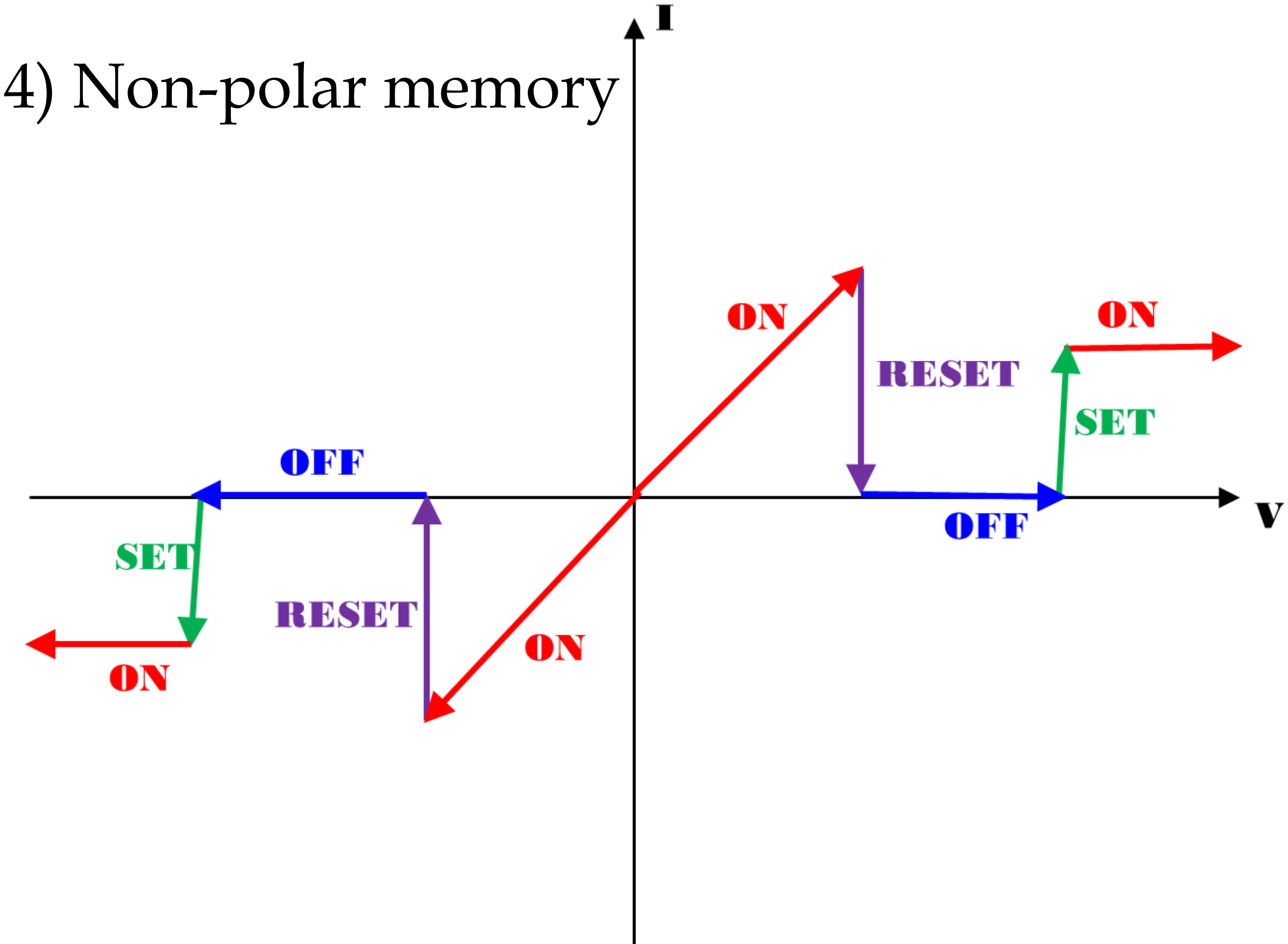
3) Bipolar memory



Organic RRAM: electrical characteristics

Typical I-V curves of **non-volatile** RRAMs

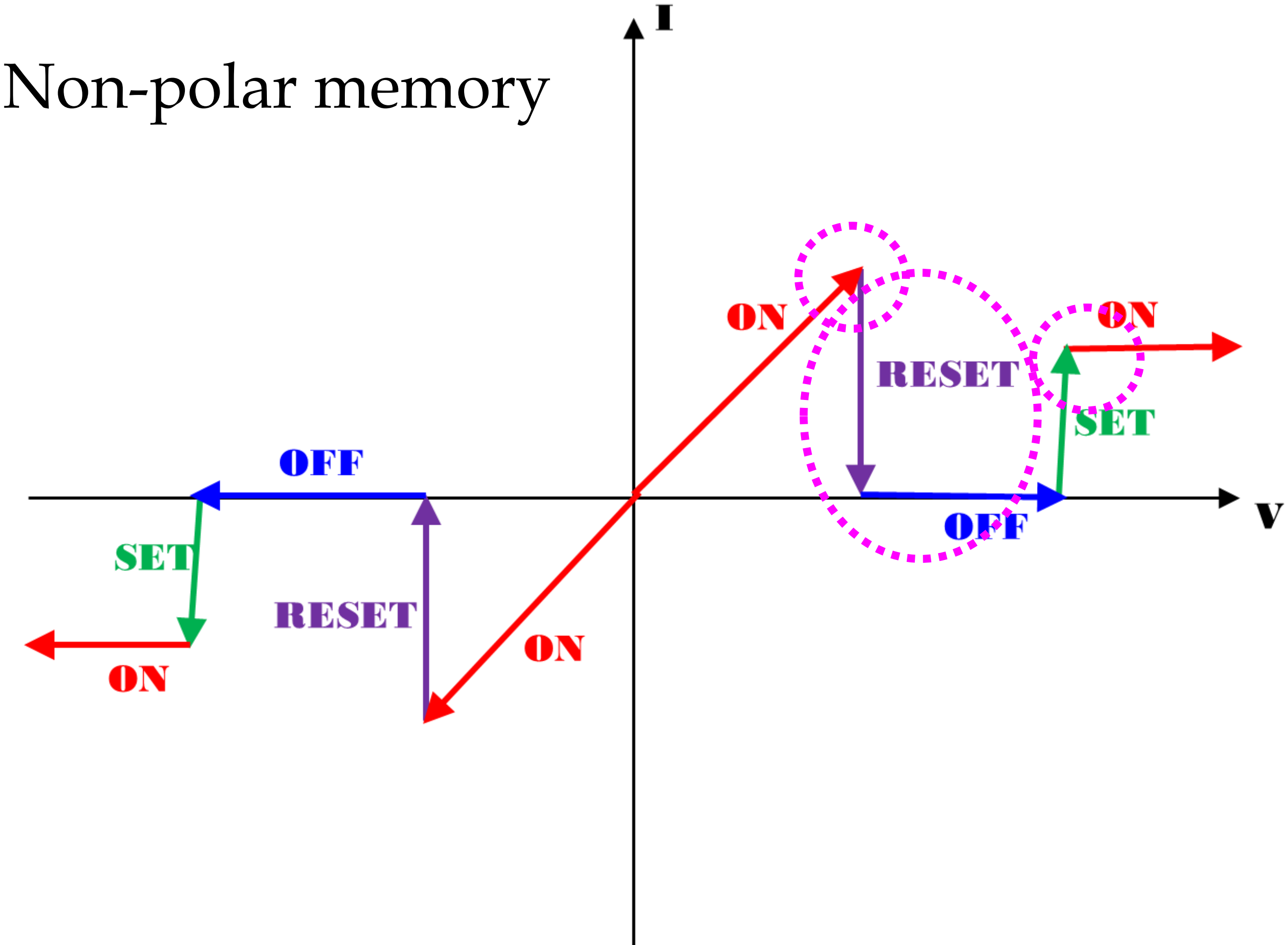
4) Non-polar memory



Organic RRAM: electrical characteristics

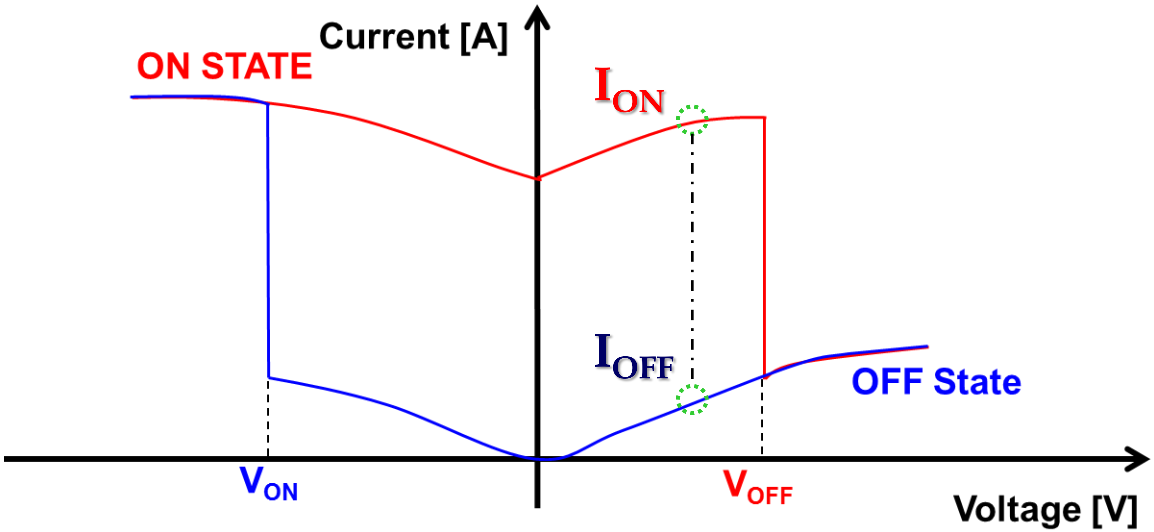
N-Shaped I-V characteristic: **Negative differential resistance (NDR)**

Non-polar memory



Organic RRAM: basic parameters

- **Operating voltage (writing , reading and erasing)**
- **ON/OFF current ratio (I_{ON}/I_{OFF}):** ratio between the current in the ON state at a voltage V and the current in the OFF state at the same voltage V



- **Retention time**: period of time the memory can retain data

Organic RRAM: conduction mechanisms

- RRAM is based on conductivity change of materials in response to the applied electric field (*non-ohmic conductivity*)
- Since conductivity is essentially a product of carrier concentration and charge mobility, non-ohmic conductivity can be induced by
  - a change in carrier concentration
  - a change in charge mobility
  - a change in both
- The electrical conduction mechanism in polymers is much more complex than in ordered inorganic materials: it cannot be explained adequately on the basis of band theory, as most polymers are amorphous in nature
- A substantial amount of research has been dedicated to understanding the switching phenomena associated with these devices
- Although the subject is still controversial, researchers have proposed several switching mechanisms based on theoretical simulations, experimental results and advanced analytical techniques

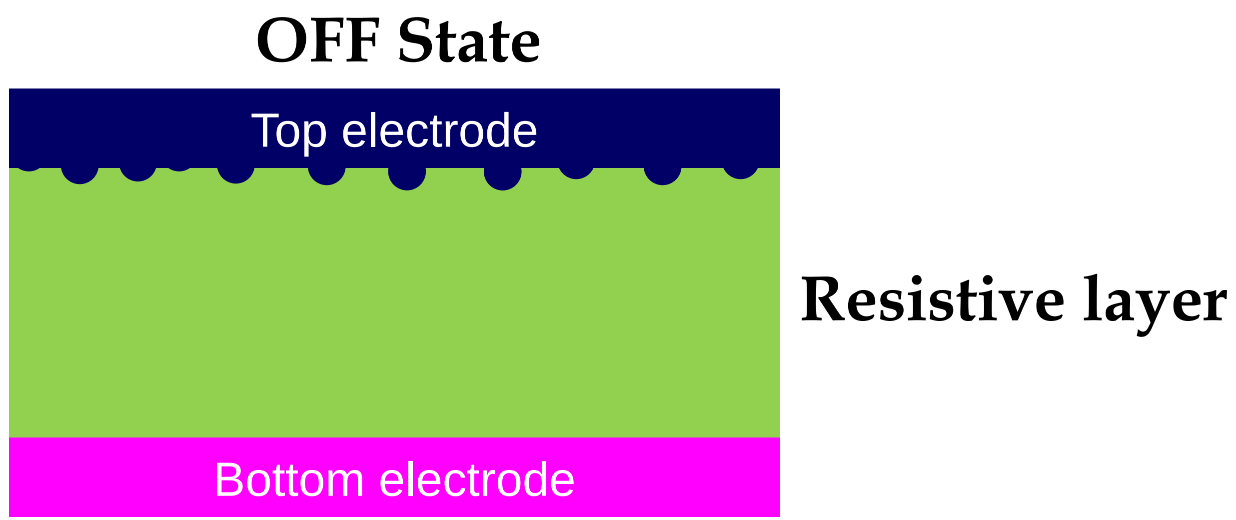
Organic RRAM: conduction mechanisms

The most widely used switching mechanisms in organic resistive memory devices:

- ✓ Filamentary conduction
- ✓ Space charge and traps
- ✓ Charge transfer
- ✓ Conformational change
- ✓ Ion conduction

Organic RRAM: Filamentary conduction

- ON state current is highly localized to a small fraction of the device area
- Electrical switching is a consequence of the formation, rupture and reformation of these filaments



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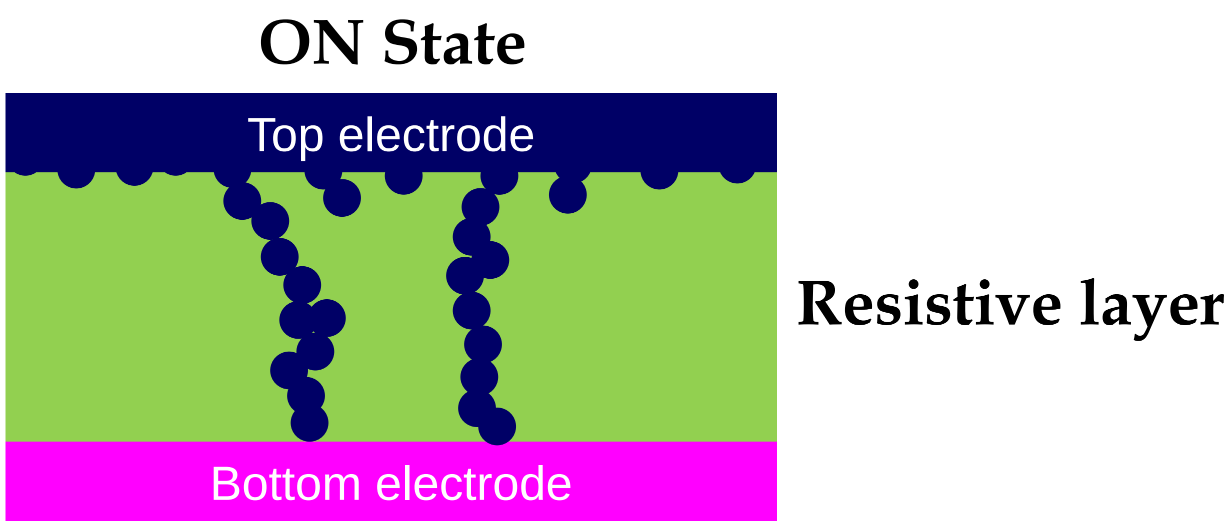

Organic RRAM: Filamentary conduction

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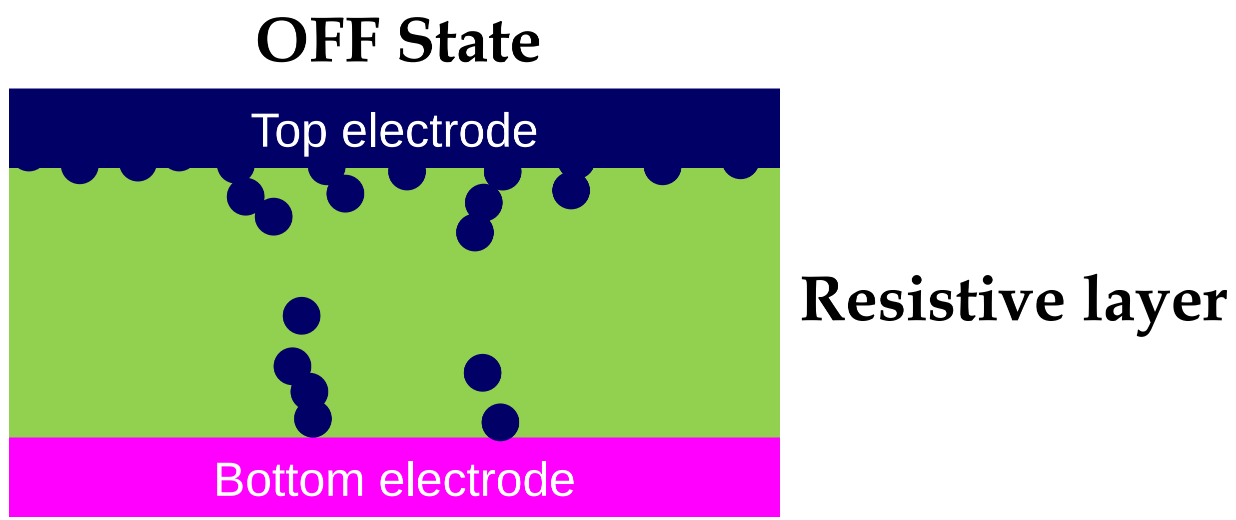
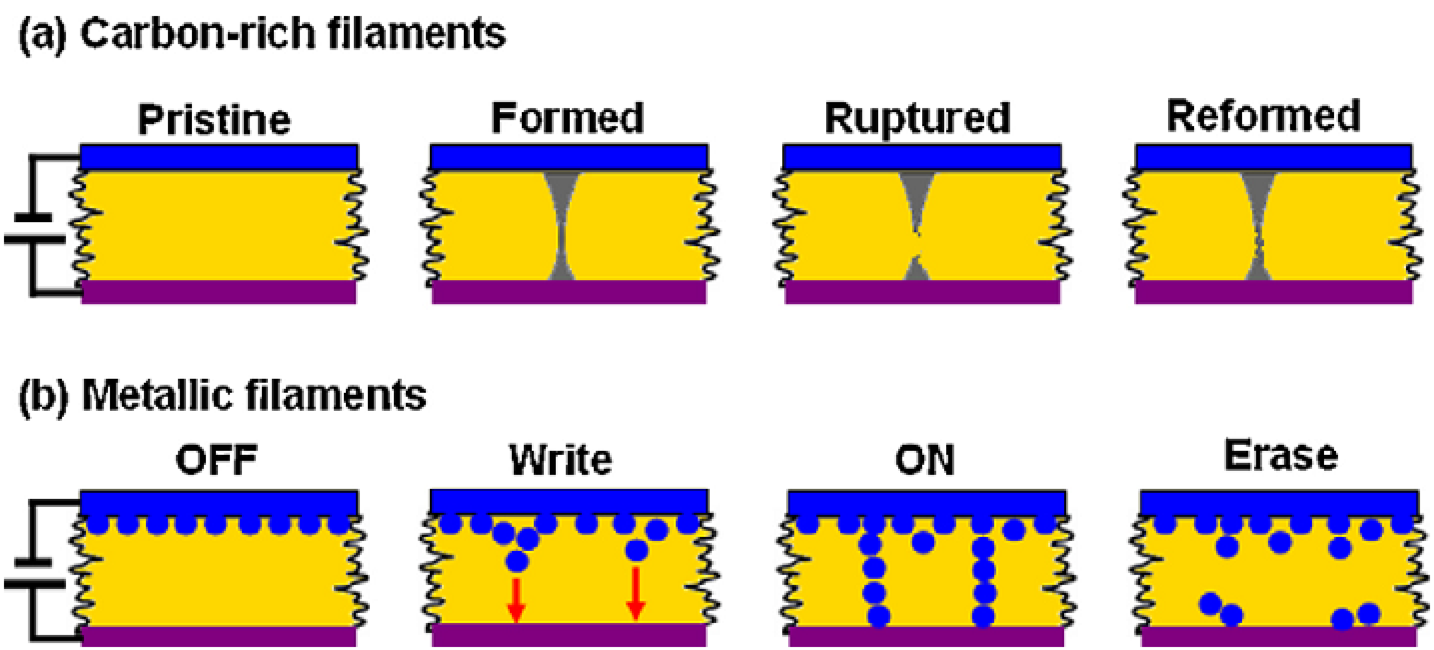


Organic RRAM: Filamentary conduction

- It is difficult to elucidate the nature of the localized conductive paths
- Two kinds of filamentary conduction have been conceptually suggested

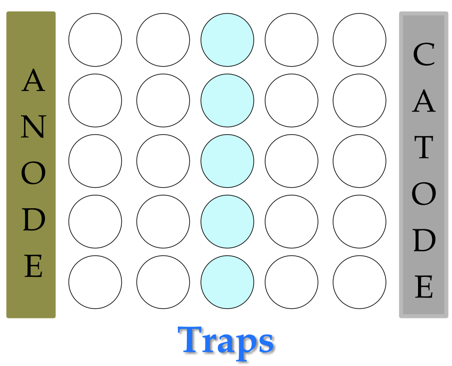


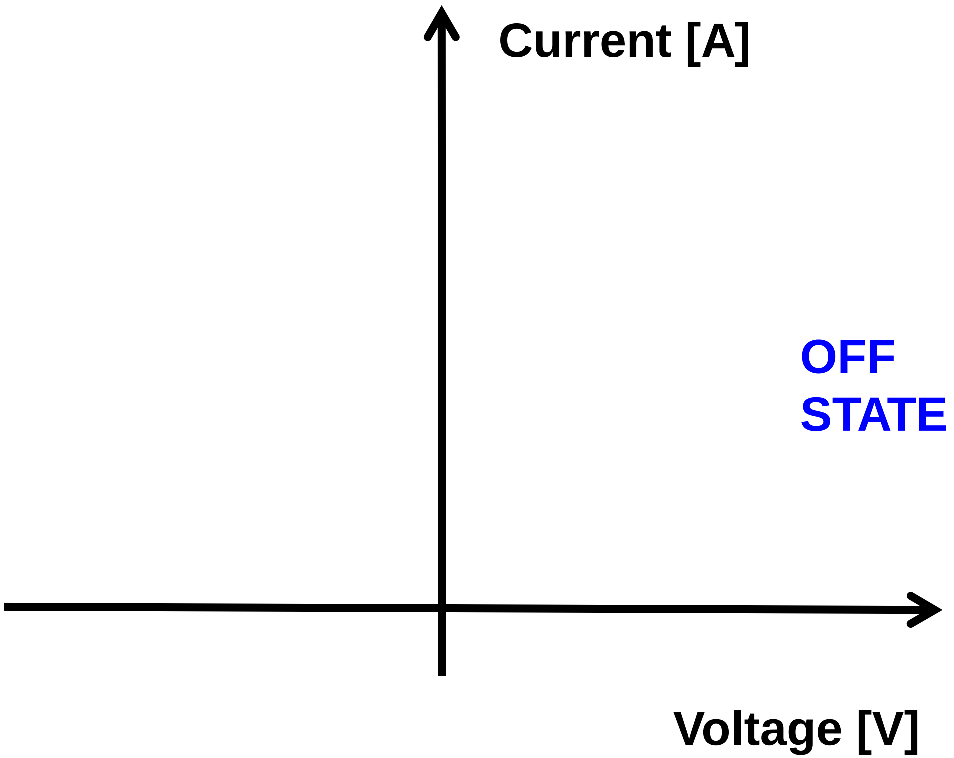
Organic RRAM: Space charge and traps

- Electrical switching behaviors of some organic materials has been reported to be associated with **space charges and traps**
- **Space charges** in materials may arise from several sources:
  - ➢ injection of electrons or holes from the electrode
  - ➢ presence of ionized dopants in interfacial depletion regions
  - ➢ accumulation of mobile ions at the electrodes interfaces
- **Traps** may be present in the bulk material or at interfaces where they will act to reduce carrier mobility. When the traps are located at interfaces, they may also affect the injection of charges into a material

Organic RRAM: Space charge and traps

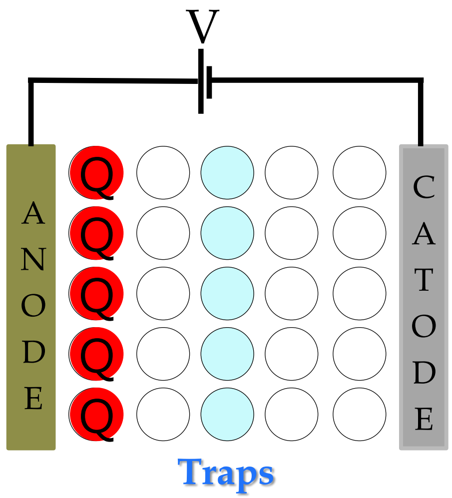
Charge trapping process

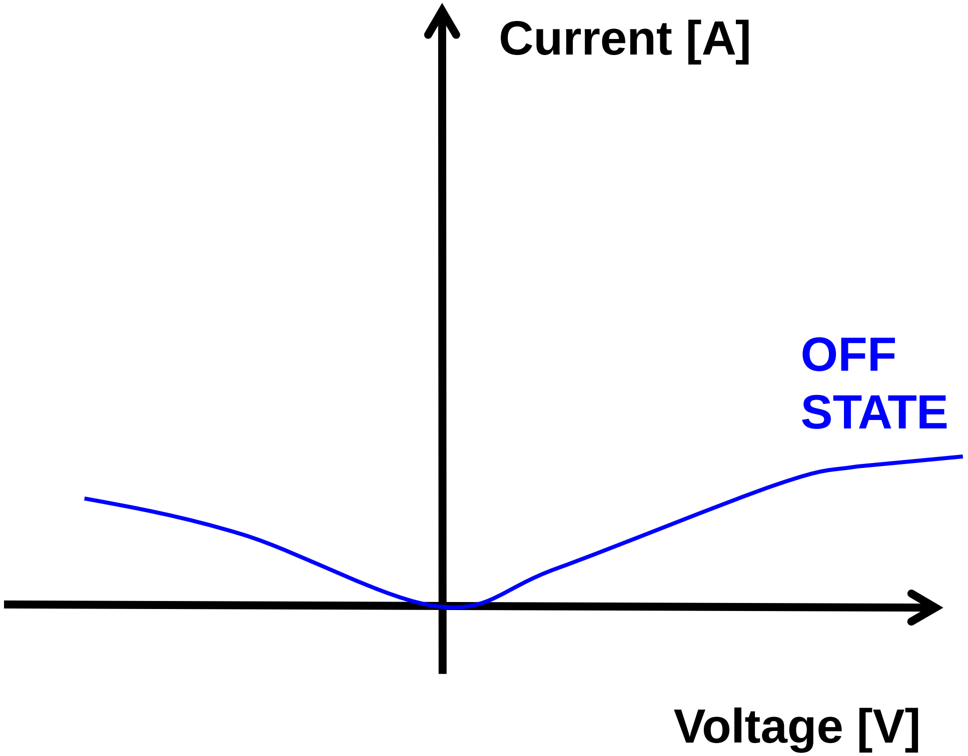




Organic RRAM: Space charge and traps

Charge trapping process

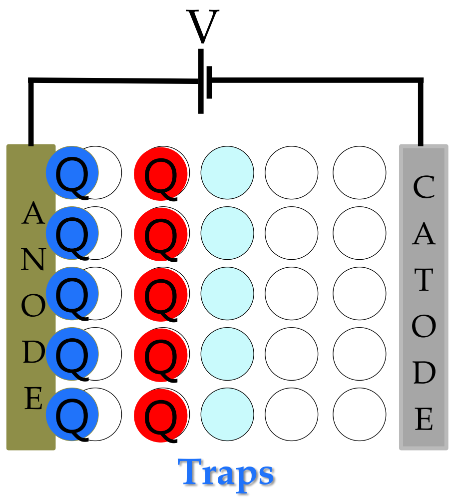


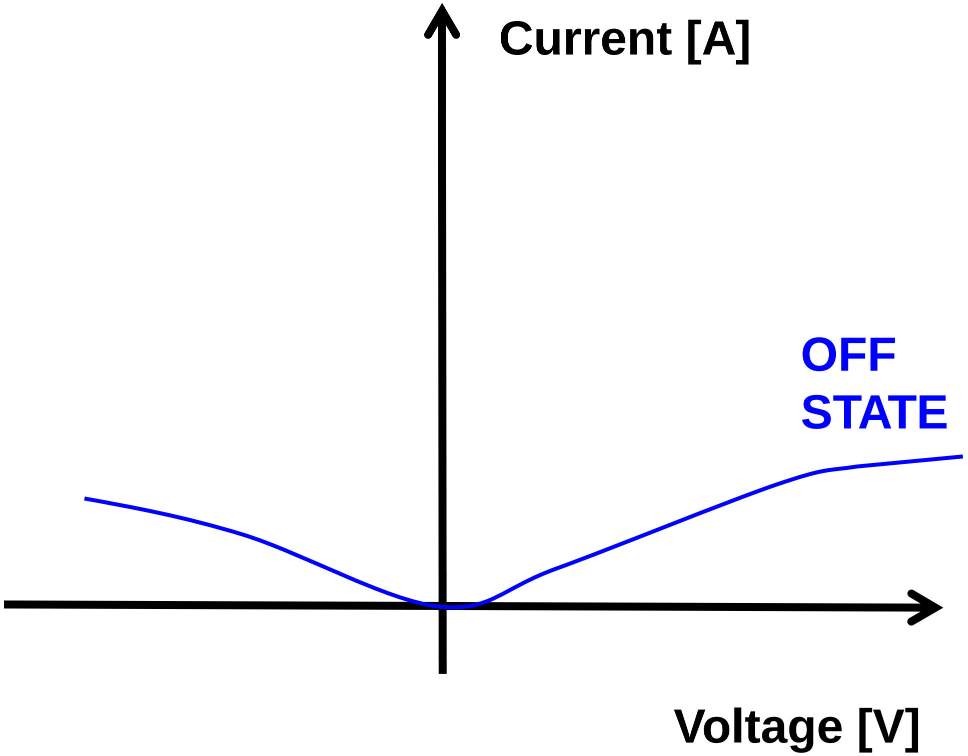


Carrier generation near the anode

Organic RRAM: Space charge and traps

Charge trapping process

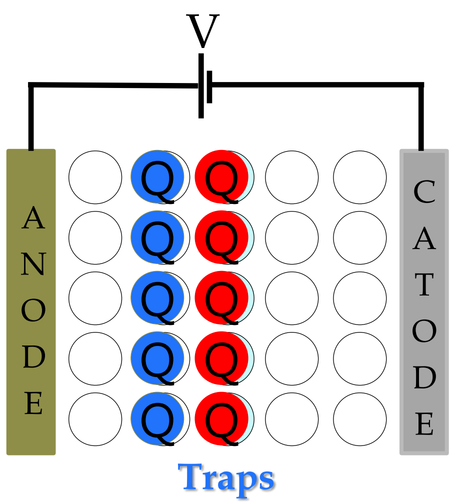


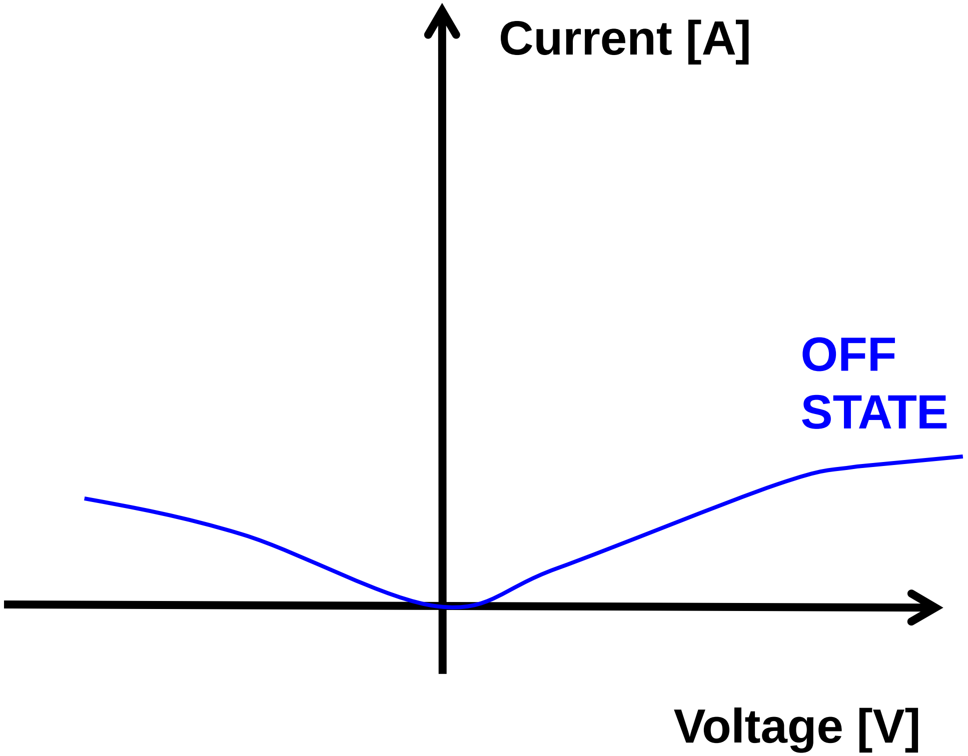


Accumulation of space charge and redistribution of the electric field

Organic RRAM: Space charge and traps

Charge trapping process

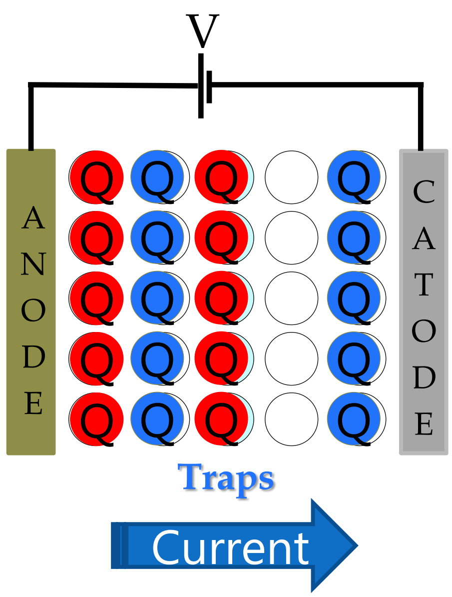


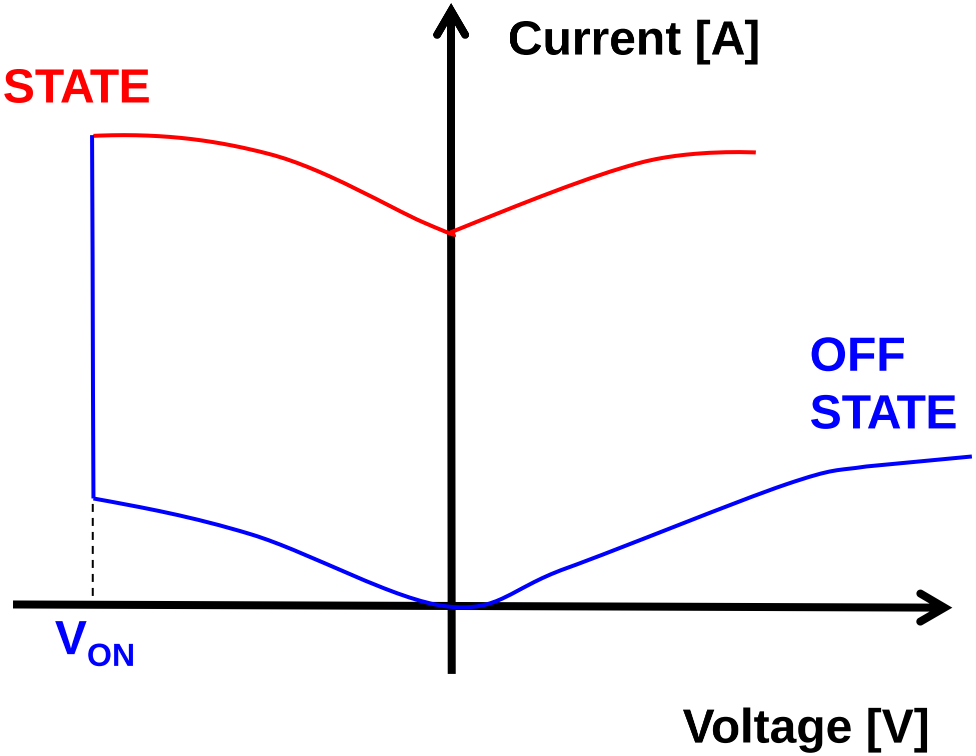


At near the turn-on voltage, the generated carriers fill some of the charge traps

Organic RRAM: Space charge and traps

Charge trapping process



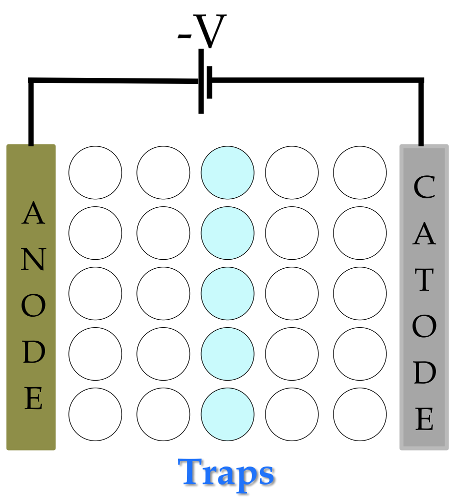


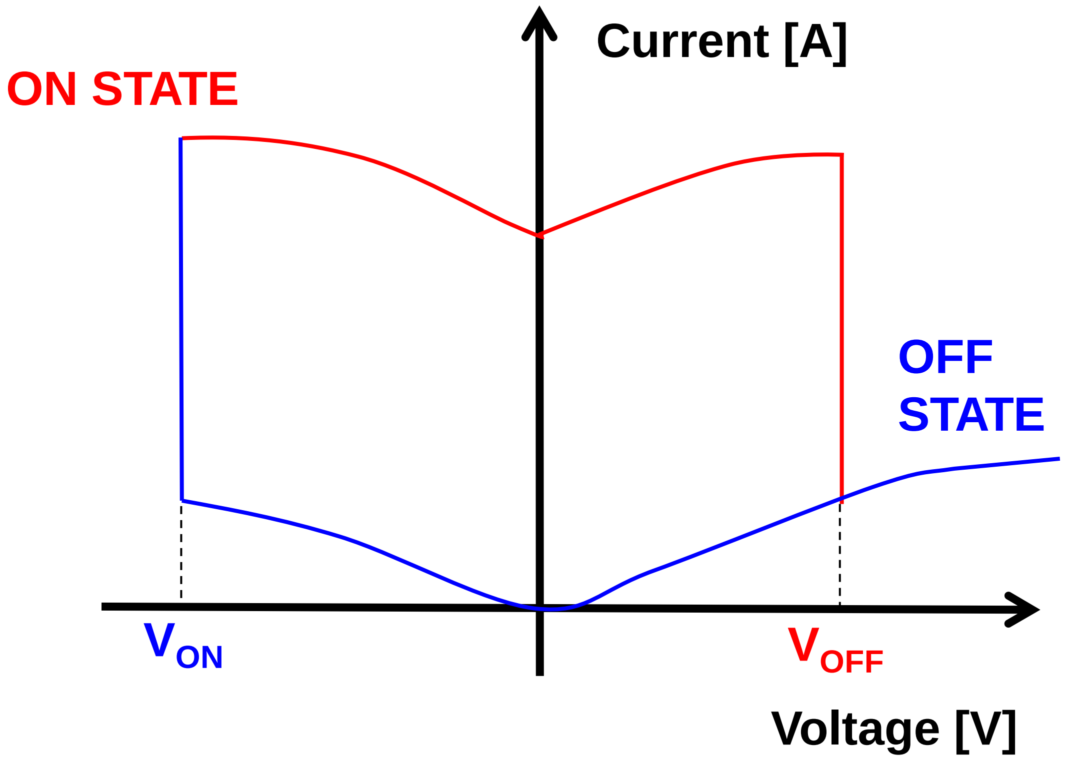
Also the cathode becomes an carrier-injecting contact , enhancing carrier concentration and mobility.

The current increases to switch the device in the ON state.

Organic RRAM: Space charge and traps

Charge detrapping process

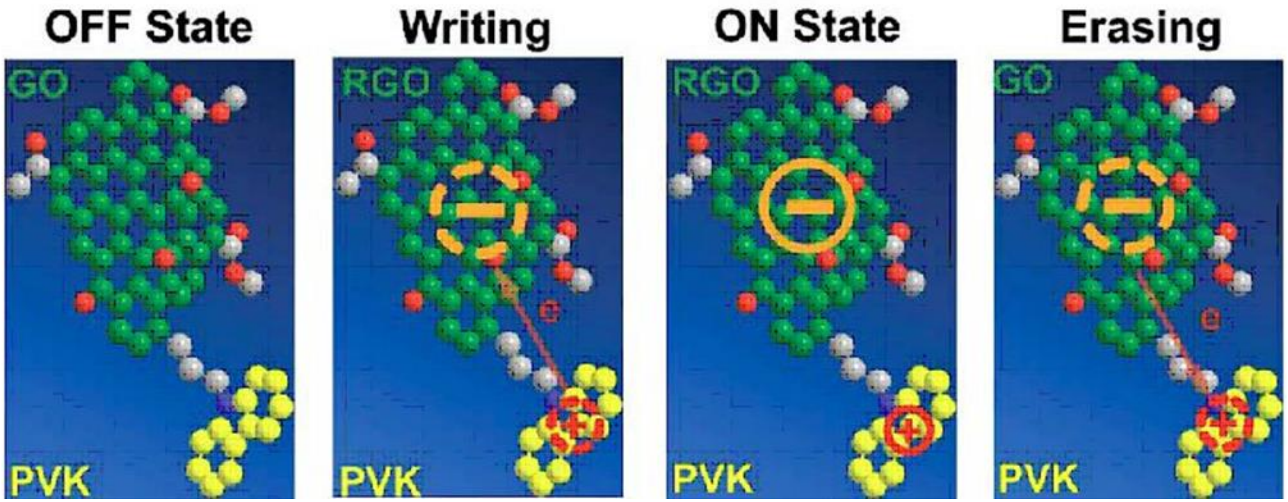




A reversed voltage pulse causes detrapping of the filled traps

Organic RRAM: Charge transfer

- **Charge transfer** (**CT**) is defined as a process of an electron donor-acceptor system in which there is a partial transfer of electronic charge from the donor to the acceptor moiety by applying an appropriate voltage, which can result in a sharp increase in conductivity.



PVK (polivinil karbazole, donor)
GO (graphene oxide, acceptor)
RGO (reduced graphene oxide)

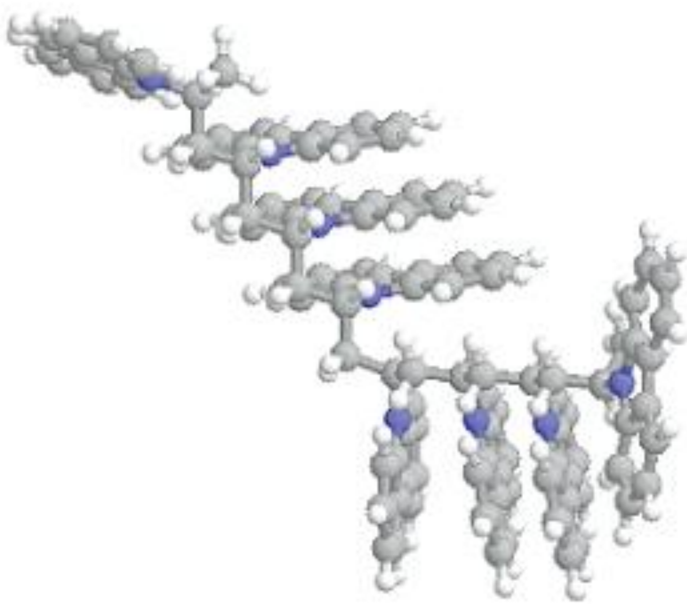
Organic RRAM: Conformational change

- A **conformational change** is a change in the shape of a flexible and dynamic macromolecule
- It can change its shape in response to changes in its environment or other factors
- Each possible shape is called a **conformation**, and a transition between them is called a **conformational change**
- Factors that may induce such changes include
  - temperature
  - pH
  - voltage
  - ion concentration.
- Resistive switching often arises from electrically induced conformational changes in molecules
- Some non-conjugated polymers can exhibit electrically induced conformational changes between a regio-random and a regio-regular structure

Organic RRAM: Conformational change

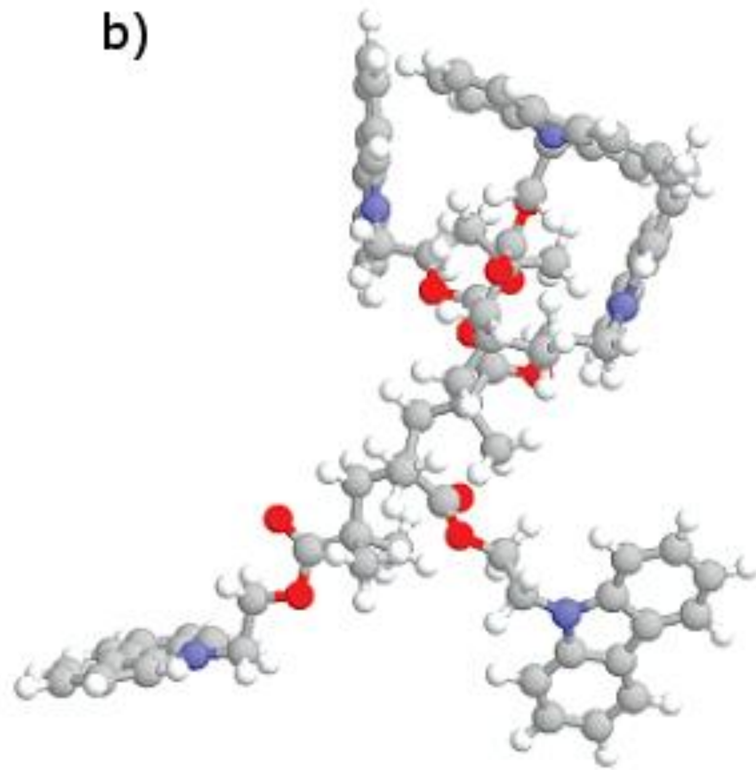
ON State

a)



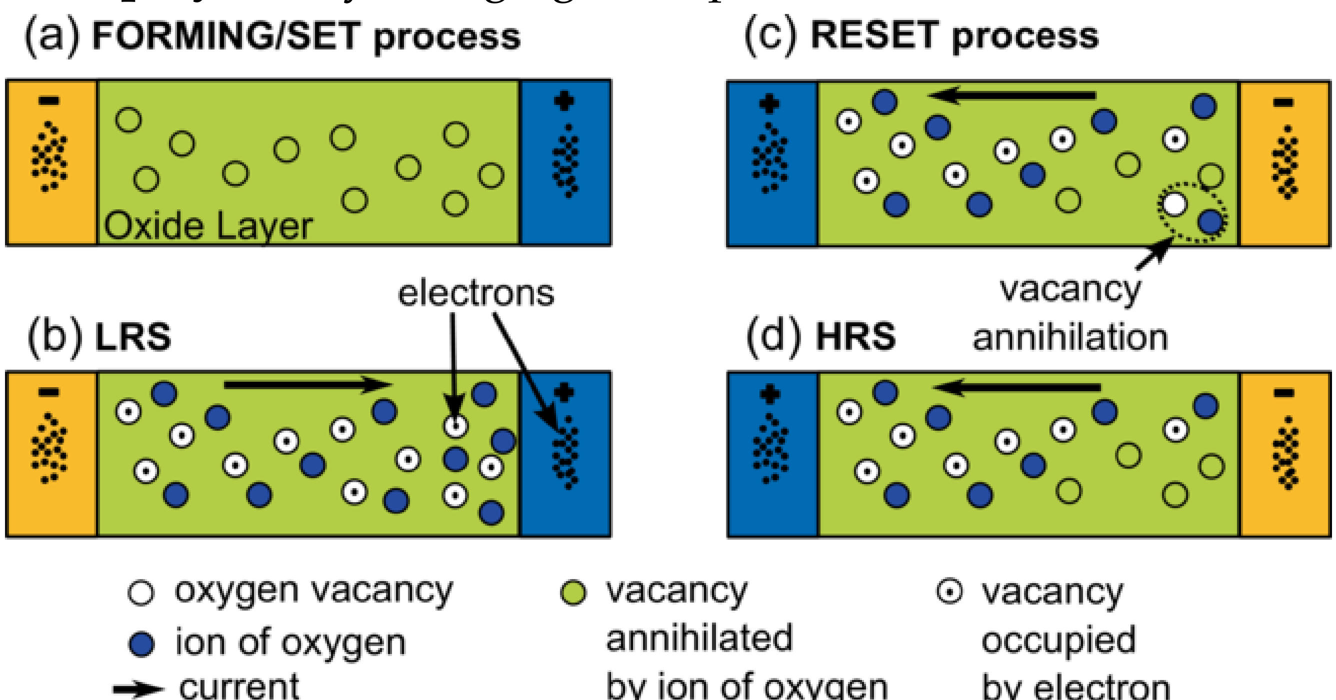
OFF State

b)



Organic RRAM: ionic conduction

- Ionic conduction occurs in polymers which contain ionic groups or to which ionic materials have been added
- Electrically rewritable memory effects can be obtained by migration of dopant ions in and out of a **polymer depletion layer at a Schottky contact**
- Memory effect can also arise from the presence of an interfacial **depletion layer at the polymer/electrode interface**
- Memory devices can be obtained inducing a conductivity change in an **electroactive polymer** by changing its dopant concentration



Progress in organic resistive memories

1968 *[Gregor, Thin Solid Films, 2(3):235–246, 1968]*
- Metal – insulator – metal (MIM) sandwich
- Resistance changes of several orders of magnitude at a voltage of 1–2 V
- Retention time in air of 30 minutes

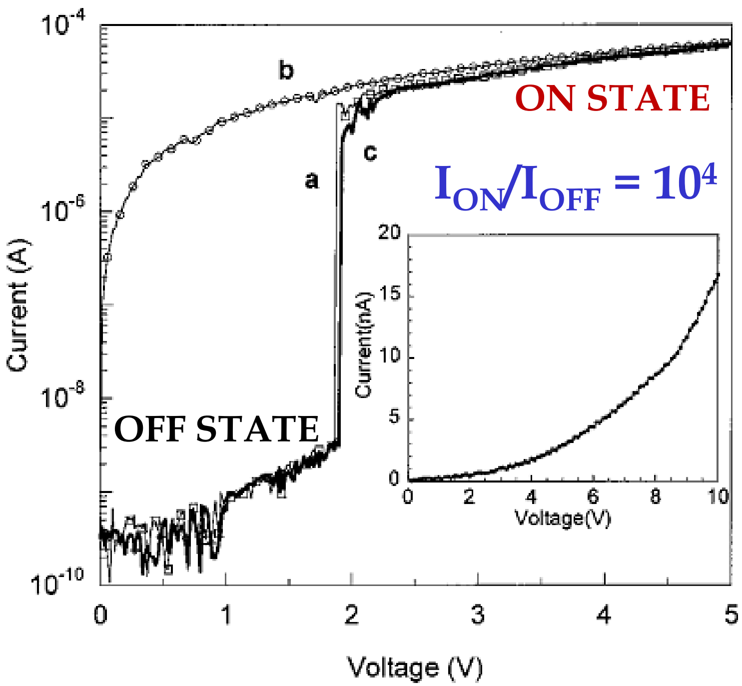
1971 *[Carchano et al., Applied Physics Letters, 19(10):414–415, 1971]*
- Reproducible bistable switching in Au-Polymer-Au junctions
- Resistance ratio > 10^7

These very early results already reveal the **experimental difficulties** associated with the **irreproducible behaviors**.
For this reason, investigation has continued over the succeeding three decades but with relatively little attention, accelerating only in recent years.

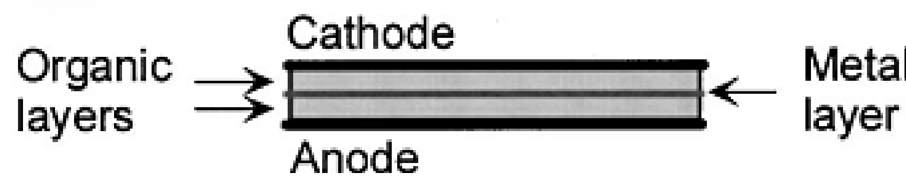
Progress in organic resistive memories

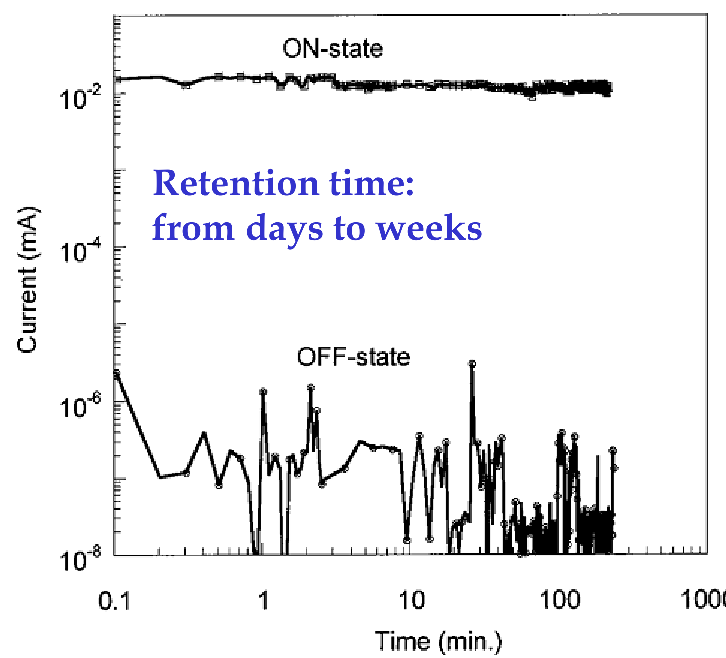
2002

- Structures first proposed by the Yang group at the University of California: an **organic/metal/organic**, triple-layer structure interposed between an anode and a cathode



L. P. Ma, J. Liu, and Y. Yang, Appl. Phys. Lett. ***2002****, 80, 2997*

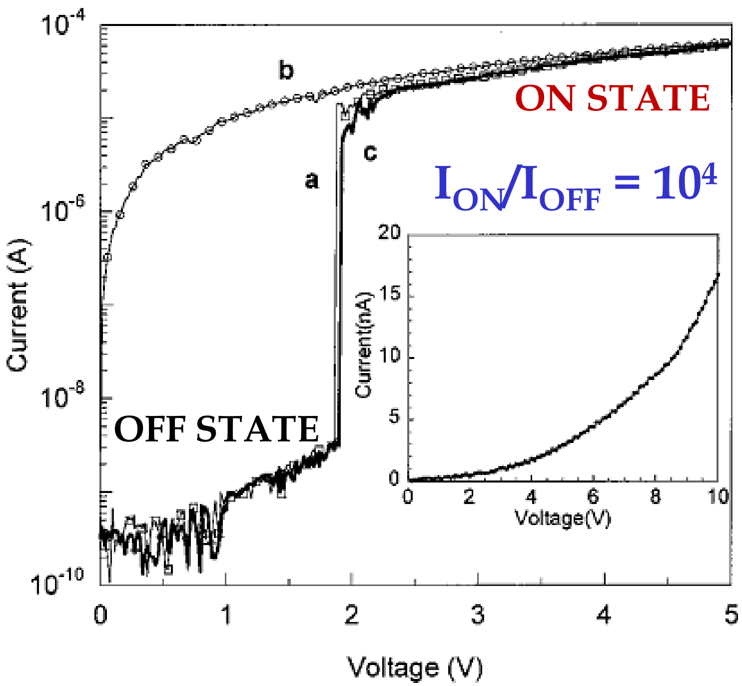


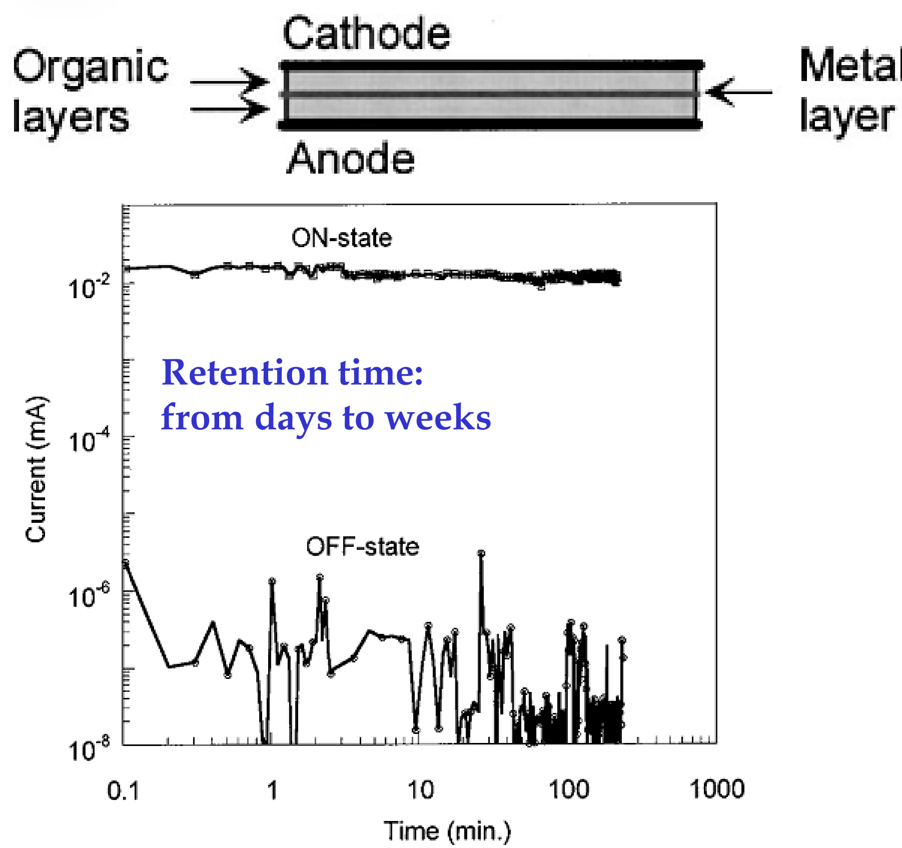


Progress in organic resistive memories

2002

As regard the mechanism behind the resistive switching, the authors suspected that **trapped charges in the middle metal layer** are responsible for the observed electrical bistability



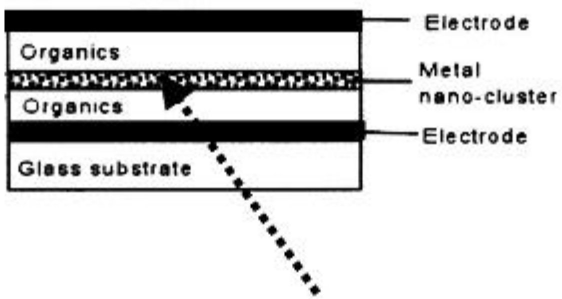


L. P. Ma, J. Liu, and Y. Yang, Appl. Phys. Lett. ***2002****, 80, 2997*

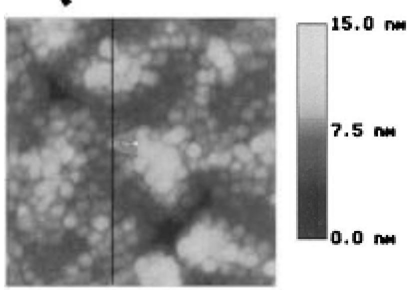
Progress in organic resistive memories

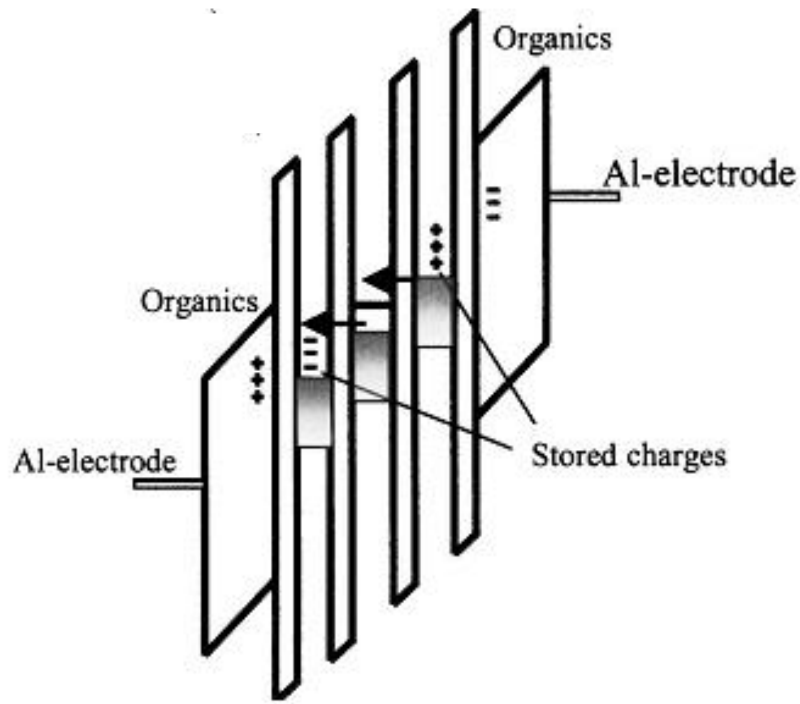
2003

- The middle metal layer for the bistable device consists mainly of partially oxidized, **small metal nanoclusters**, instead of pure metal, as previously described



AFM image of the middle metal clusters





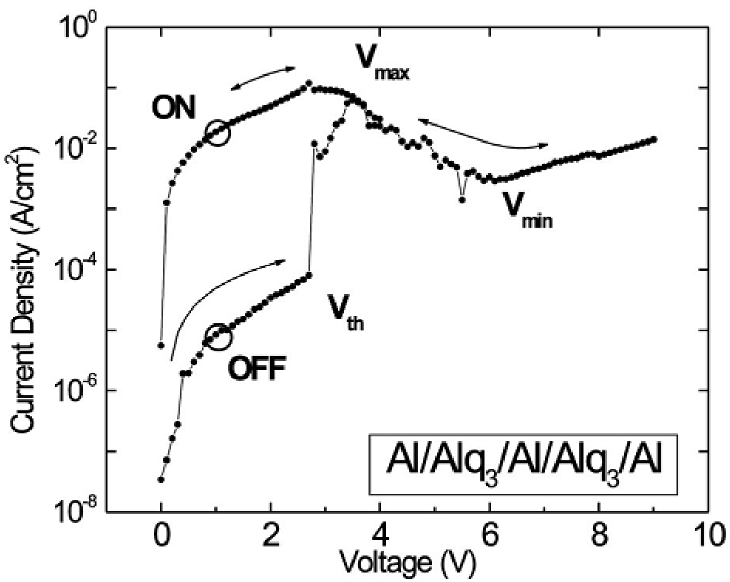
Schematic energy band diagram

L. P. Ma, S. M. Pyo, J. Y. Ouyang, Q. F. Xu, and Y. Yang, Appl. Phys. Lett. ***2003****, 82, 1419*

Progress in organic resistive memories

2004

- The **mechanisms for bistability** in these devices were thoroughly investigated by Bozano et al.
- They proposed that the resistive switching phenomenon observed in organic layers containing granular metal particles conforms to a **charge storage mechanism**



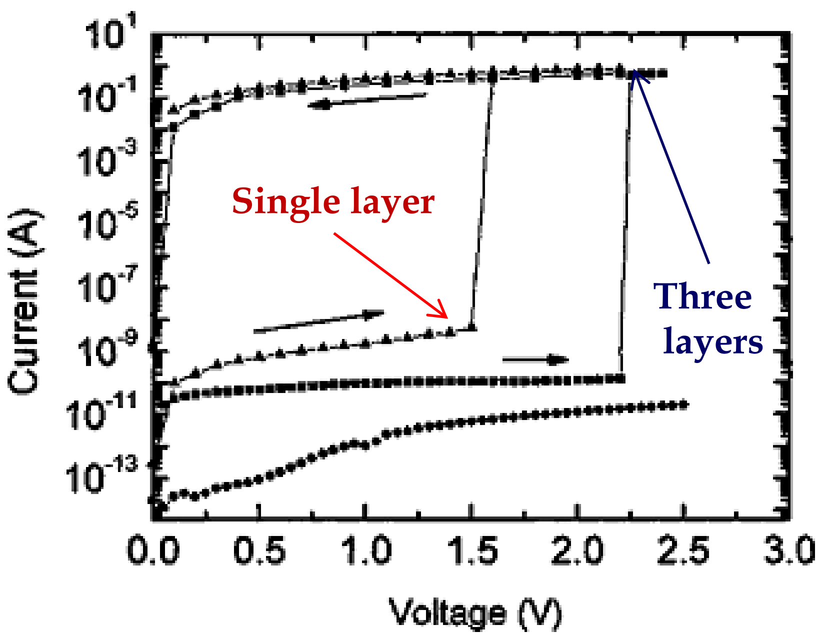
L. D. Bozano et al., Appl. Phys. Lett. 2004; 84: 607-9

- The **mechanism** is **very general** and many other material combinations show similar behavior
- The mechanism responsible for the bistable resistance behavior of these devices is **charge trapping and space-charge** field inhibition of injection
- A **discontinuous, granular layer** is critical to the bistability of the device
- Trapping properties can be tailored by the choice of metal, the size of particles and their position in the device structure

Progress in organic resistive memories

2004

- At the same time Tondelier et al. report a bistable organic memory made of a **single organic layer** embedded between two electrodes
- They found that one-layer and three-layer organic bistable devices exhibit similar current–voltage characteristics



*Tondelier et al., Applied Physics Letters, 85(23):5763–5765, **2004**.*

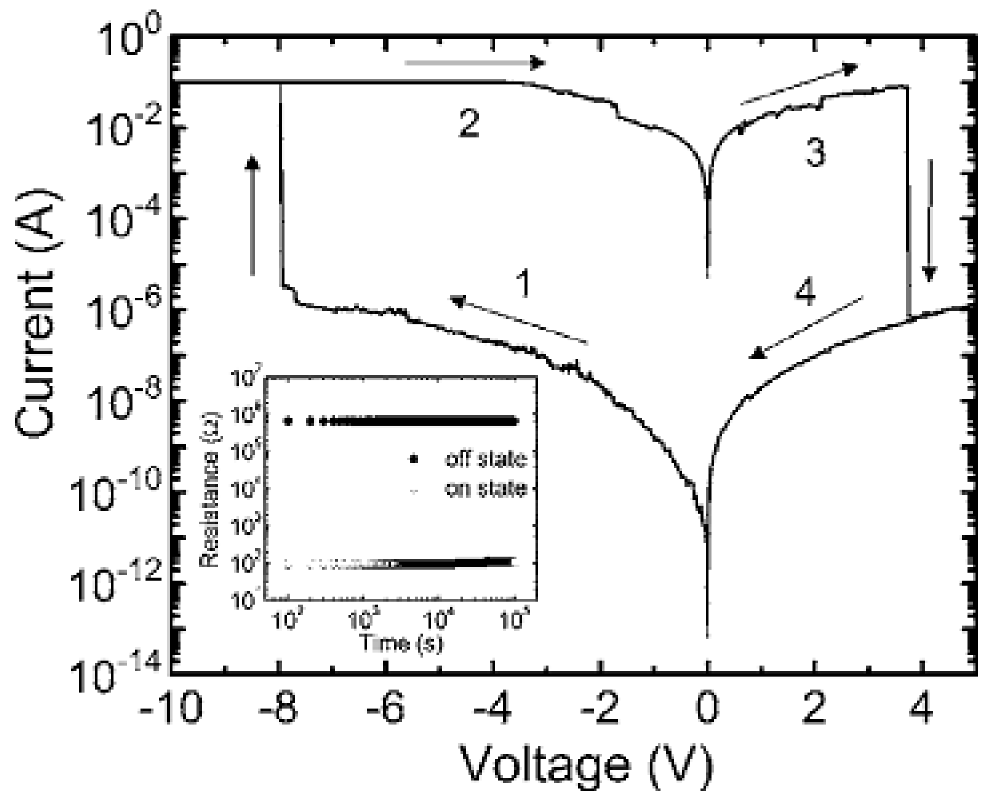
- They observed on-state current over off-state **current ratios** as large as **10^9**
- This behavior was attributed to the inclusion of metal nanoparticles into the organic material during the top electrode evaporation for both types of devices, with **metallic filaments of nanoparticles** forming in the polymer under high electric fields, giving rise to a high conductivity ON state.

Progress in organic resistive memories

2005

- Progression in terms of perfomance were obtained by Lai et al., who demonstrated bistable resistance switching characteristics of an Aluminum/poly(N-vinylcarbazole) (PVK)/Aluminum structure

- Reproducible resistance switching
- Large **ON/OFF ratio** of **10^4**
- **Retention time** of about **10^5** sec (27 hours) in ambient conditions
- Mechanism is explained on the basis of the **filament theory**

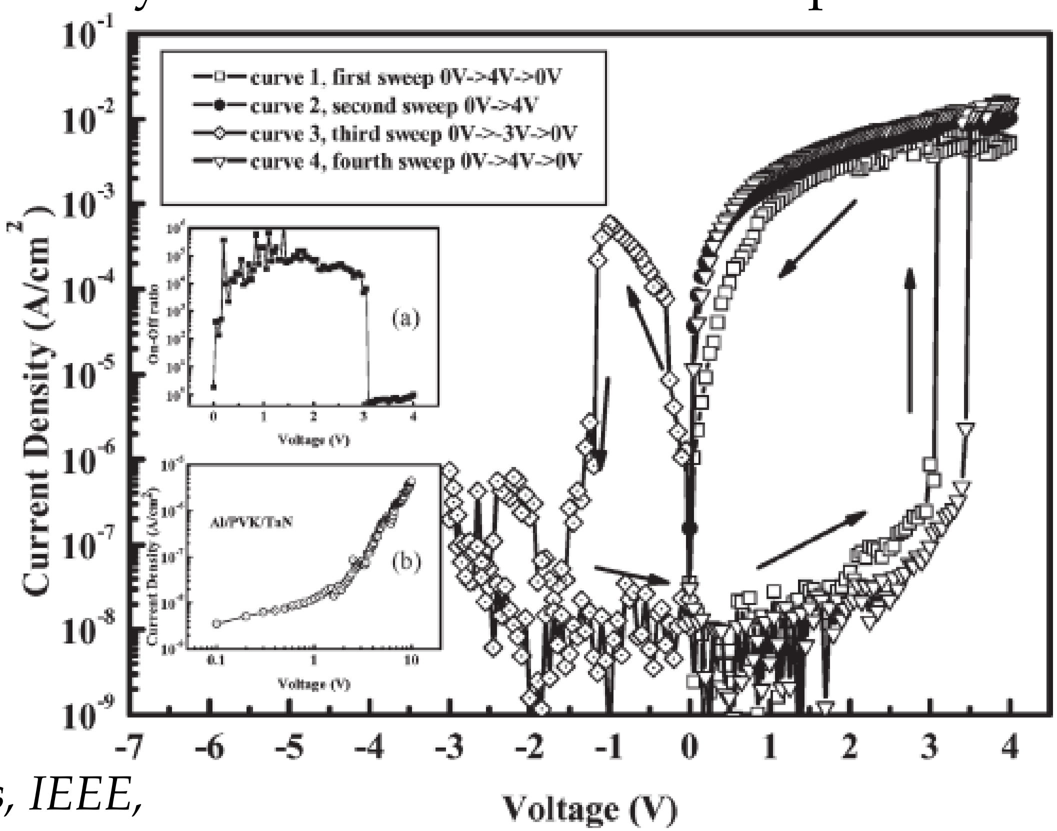


Lai et al., Applied Physics Letters, 87(12):122101, ***2005****.*

Progress in organic resistive memories

2007

- Bistable device based on PVK mixed with gold nanoparticles (GNPs), which serve as the active layer between two metal electrodes.
- Electrical bistability and memory effect are due to the incorporation of GNPs in the PVK



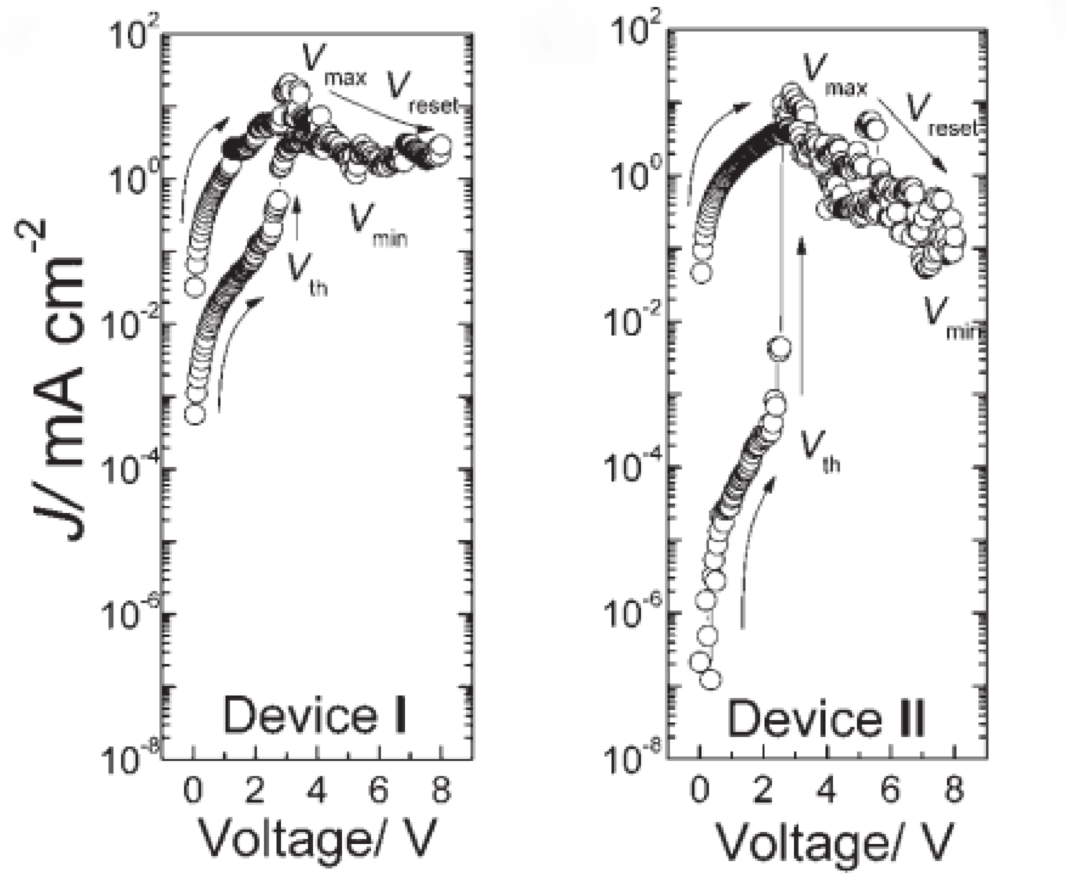
- PVK serves both as the matrix for GNPs and electron donor since it has a strong capability to provide electrons
- GNPs act as electron acceptors
- ON/OFF current ratio as high as 10^5

Song et al., Electron Device Letters, IEEE, 28(2):107–110, ***2007***

Progress in organic resistive memories

2008

- PVK was also used embedded between an Al electrode and ITO modified with Ag nanodots (Ag-NDs)
- Ag-NDs act as trapping sites
- **Retention time** of **3 days**
- **ON/OFF** current ratio of $\mathbf{10^4}$



- **Device I: Without Ag-NDs**
- **Device II: With Ag-NDs**

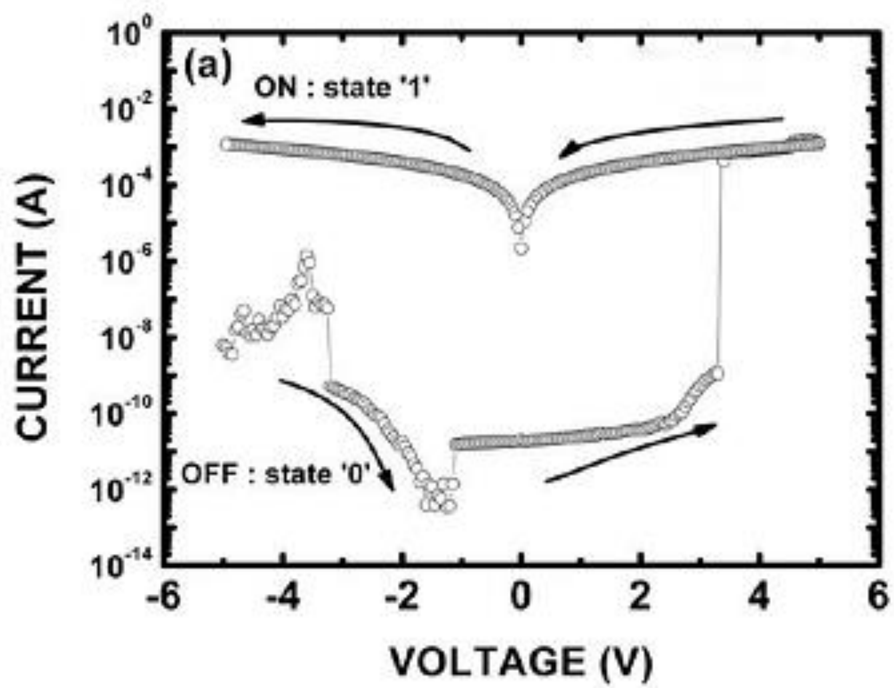
Kondo et al., Advanced Functional Materials, 18(7):1112–1118, ***2008***

Progress in organic resistive memories

2010

- Flexible non-volatile organic bistable devices fabricated with graphene sandwiched between two insulating poly(methyl methacrylate) (PMMA) polymer layer

- Bistable behavior might be attributed to conducting filaments formed in the PMMA layer at the state transition
- The graphene layer and the intrinsic trap states of PMMA act as trapping sites, which capture electrons injected from the electrode, generating a conducting filament in the PMMA layer
- **Retention time** of **10^5 sec** (27 hour) in ambient conditions
- **ON/OFF** current ratio of **10^7**



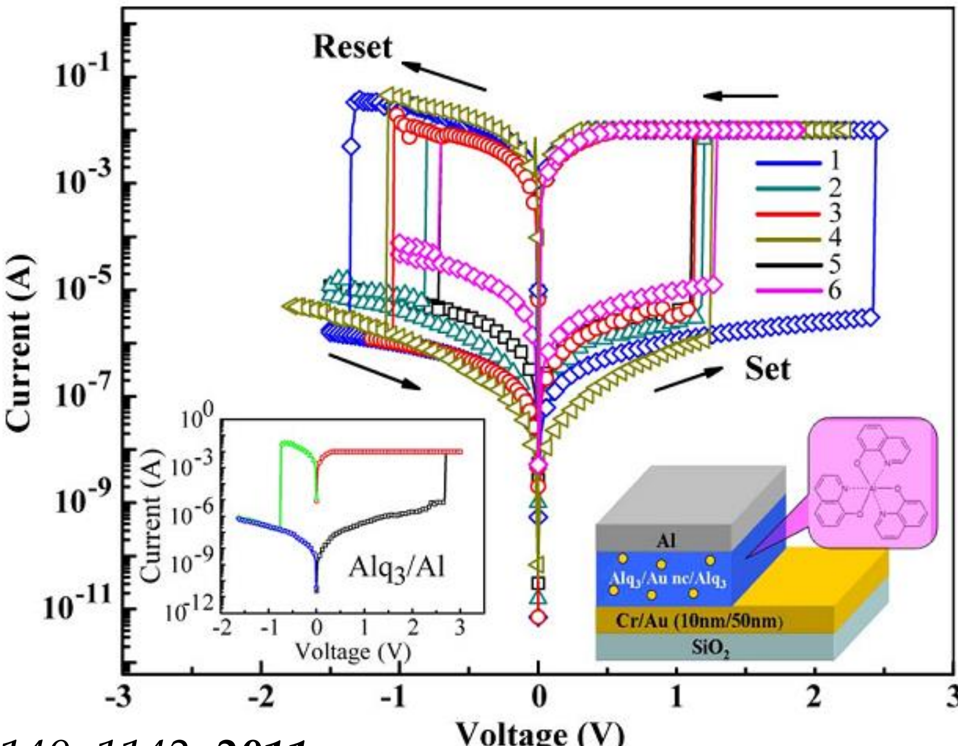
Son et al., Nano Lett. **2010**,10, 2441-2447

Progress in organic resistive memories

2011

- Organic non-volatile memories with structure Au/Alq_3/metal nanoparticles (Au or Al)/ Alq_3/Al
- Electrical characteristics of devices with gold NPs display much better performances with respect to those with aluminum NPs

- **ON/OFF** current ratio ~ **10^4**
- **Retention time ~ 4 h**
- Conduction mechanism of the devices was demonstrated to be **charge trapping:** at low voltages the conduction is dominated by intrinsic carriers of the organic material. In this region, the deep traps are mostly empty. As the bias increases, the deep traps are gradually filled, and the device turn into ON state, and a sharp increase of current density is observed.



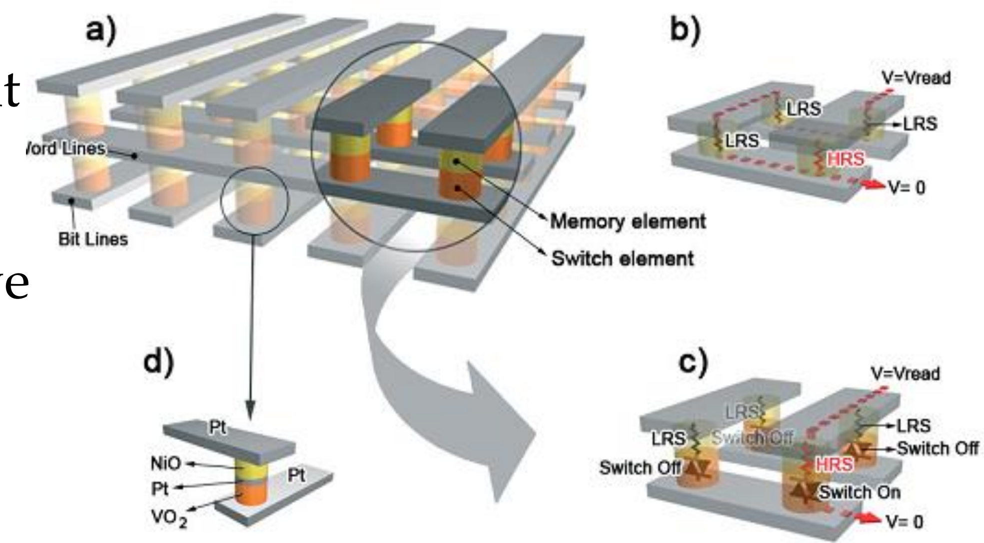
*Liu et al., Electron Device Letters, IEEE, 32(8):1140–1142, **2011**.*

Memory performance enhancement

- The switching characteristics of organic resistive memory devices are strongly influenced by the **properties of interfaces and active materials**: various approaches to control and optimize these switching properties
- **Interface between an electrode and an organic material** influences the charge injection barrier: the simplest method for modulating this interface is to **change the type of electrodes**
- Resistive switching in polymer-metal nanoparticle films can be tuned by **changing the work function of the electrode**: introducing additional layers at the metal–polymer interfaces is an effective strategy for controlling the mobility or number of charge carriers that pass through organic devices
- **Charge conduction** through a device is often strongly **governed** by the **surface morphology** of an organic film: the morphology of the organic layer should be carefully controlled to produce excellent non-volatile memory effects

Architectural concepts for advanced memory devices

- The **cross-talk phenomenon** in memory cells often occurs due to parasitic leakage paths (called **sneak paths**) through neighboring cells with low resistances in cross-bar array structures
- These phenomena disturb the reading process in selected cells, which must be eliminated in practical memory applications
- To solve the crosstalk problem, a **switching element** (diode or transistor) can be added to each memory cell
- One diode-one resistor (**1D-1R**) or one transistor-one resistor (**1T-1R**) architectures improve reading accessibility without disturbing the reading process
- **1D-1R** is **preferred** because it occupies less area and fabrication is simpler
- Different 1D-1R systems have recently been developed

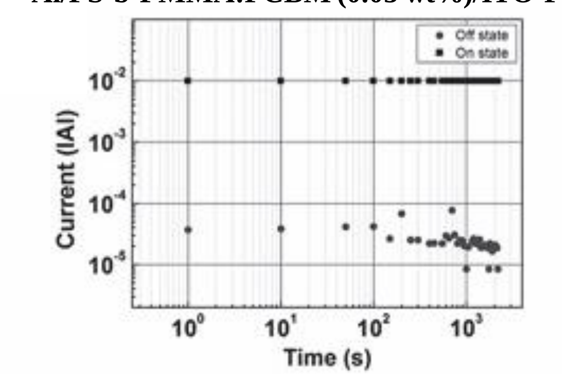


Lee et al., Adv. Mater.2007,19, 3919–3923

Organic RRAM: delopmental status

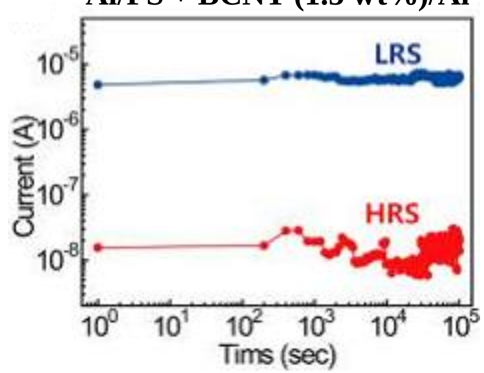
- ✓ Remarkable progress in the advancement of novel memory technologies in recent years
- ✓ Some significant challenging tasks to be resolved for practical application:
  - ➢ Complete understanding of the resistance switching mechanisms
  - ➢ Improvement of device reproducibility and reliability
  - ➢ Development of devices with long term stability for employment in ambient atmosphere
    - ❖ many devices show excellent behaviors but only in inert atmosphere
    - ❖ only few devices show a reproducible bi-stable behavior under ambient atmosphere:

Al/PS-b-PMMA:PCBM (0.05 wt%)/ITO PET



Jo et al., Macromol. Rapid Commun. 2013, 34, 355−361

Al/PS + BCNT (1.5 wt%)/Al

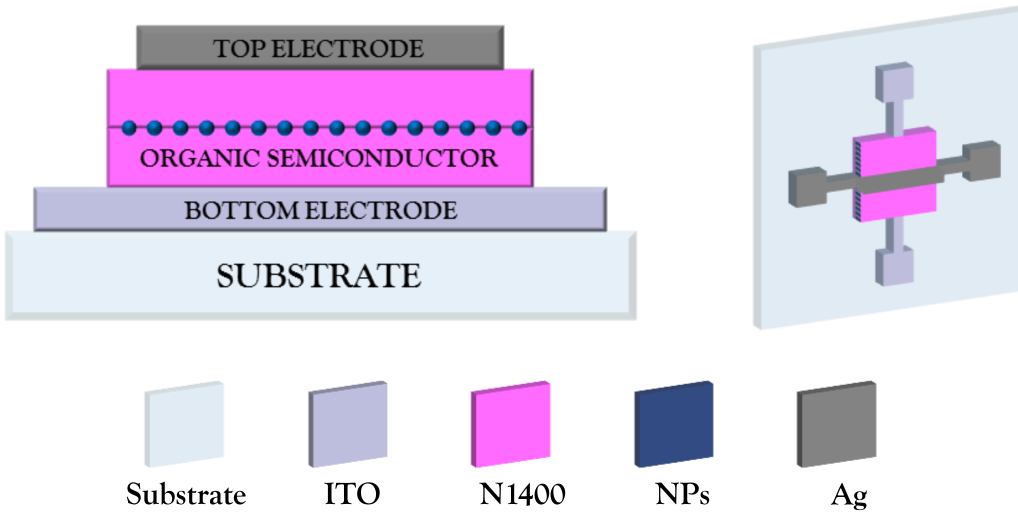


Hwang et al., Nano Lett.2012, 12, 2217−222

Maximum retention time in air in the order of 10^5 s (~1 day)

A novel organic resistive memory

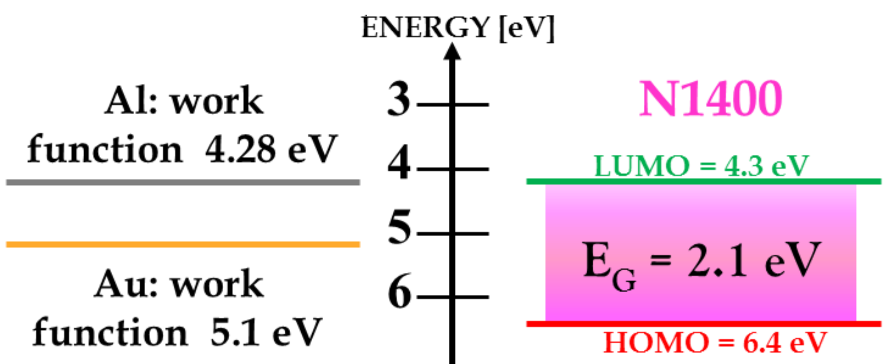
Materials and schematic

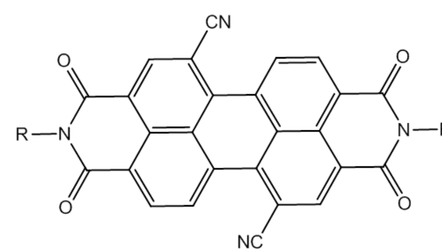


A new combination of materials

- ITO bottom electrode
  - ✓ transparent electrical conductor
  - ✓ Work function: 4.4-4.5 eV
- Ag top electrode
  - ✓ Work function: 4.26 eV
- ActivInk™ N1400 as semiconductor
  - ✓ N-type
  - ✓ Small molecule
  - ✓ Stable performances in ambient conditions

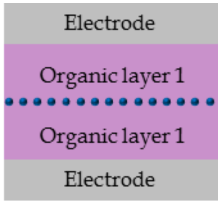
Two kinds of metal nanoparticles





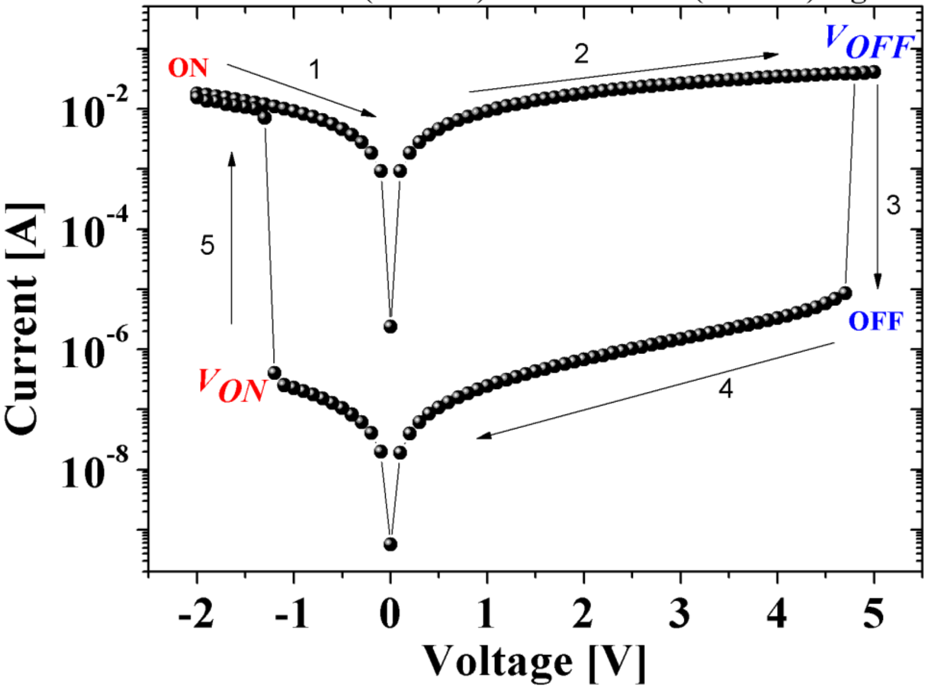
ActivInk™ N1400

A novel organic resistive memory: electrical characterization in air



Gold Nanoparticles

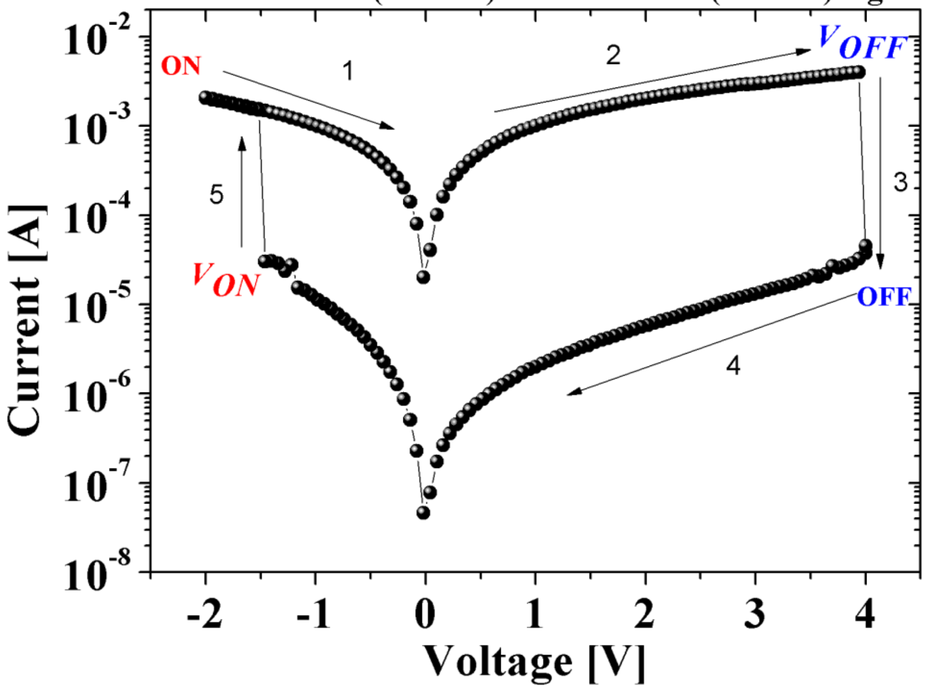
ITO/N1400(120 nm)/Al NPs/N1400(120 nm)/Ag



Parameter	Average ± error
V_{WRITE} [V]	-1.6± 0.4
V_{ERASE} [V]	+3.1 ± 0.6
I_{ON}/I_{OFF}	$(4 \pm 1)\cdot 10^3$

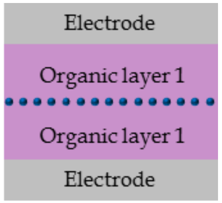
Aluminum Nanoparticles

ITO/N1400(120 nm)/Au NPs/N1400(120 nm)/Ag



Parameter	Average ± error
V_{WRITE} [V]	-1.4± 0.4
V_{ERASE} [V]	+5 ± 1
I_{ON}/I_{OFF}	$(3 \pm 1)\cdot 10^4$

A novel organic resistive memory: electrical characterization in air



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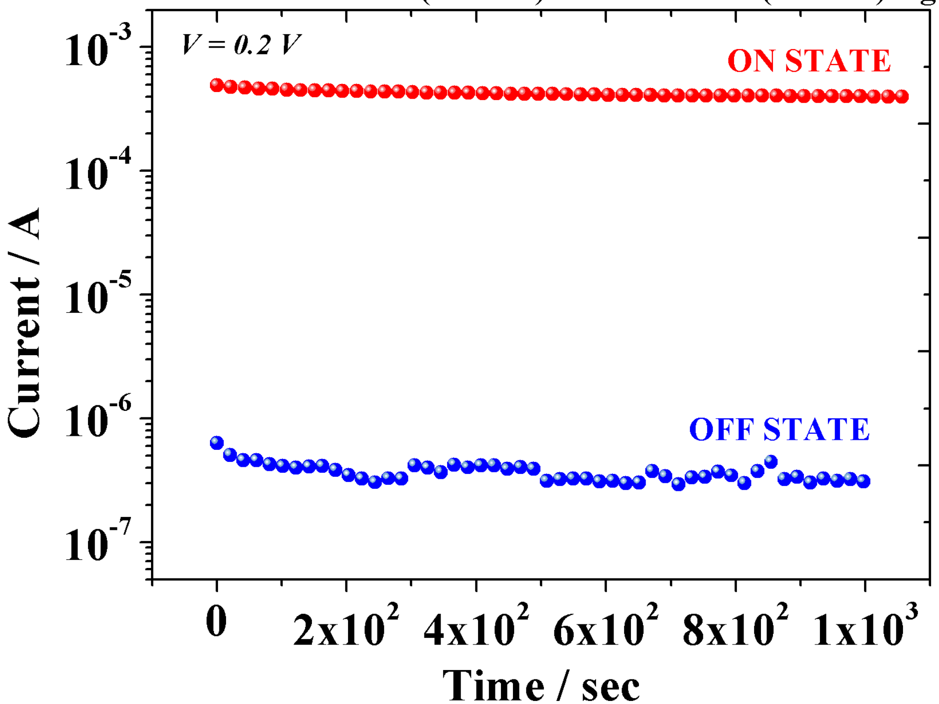

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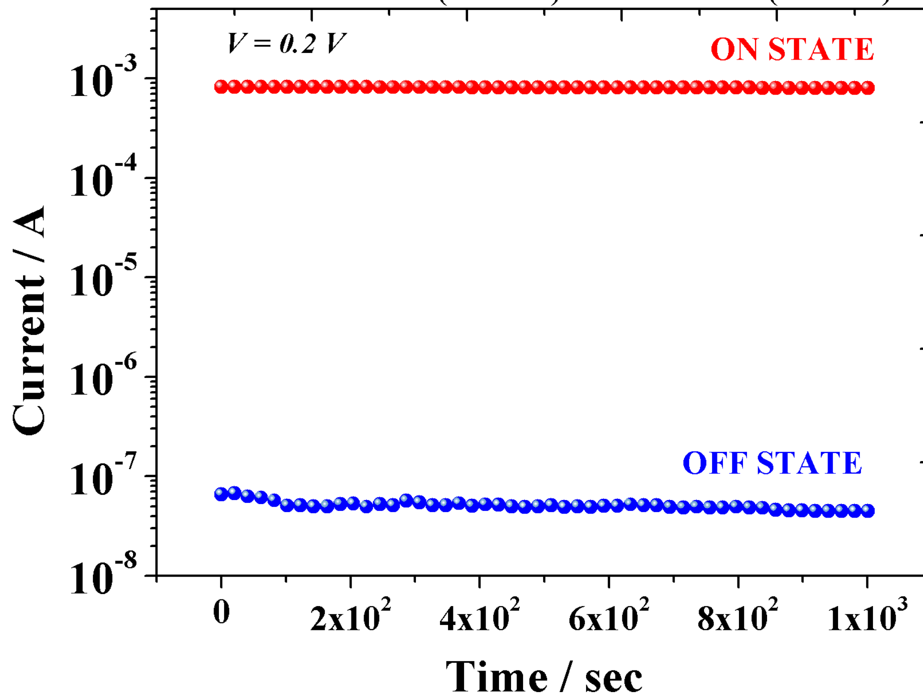

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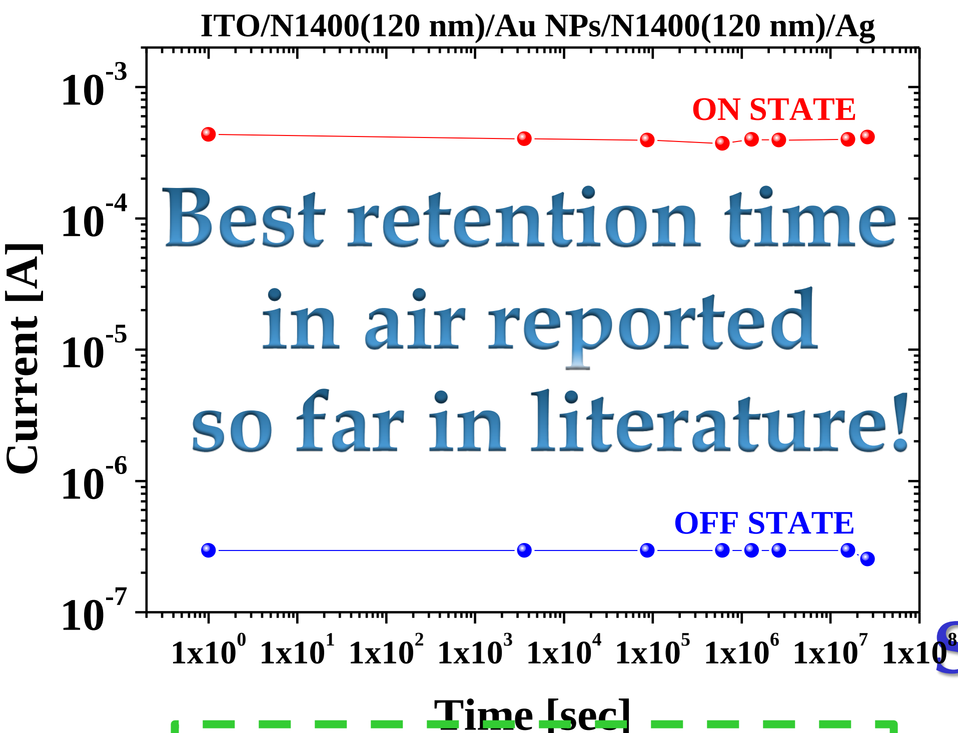
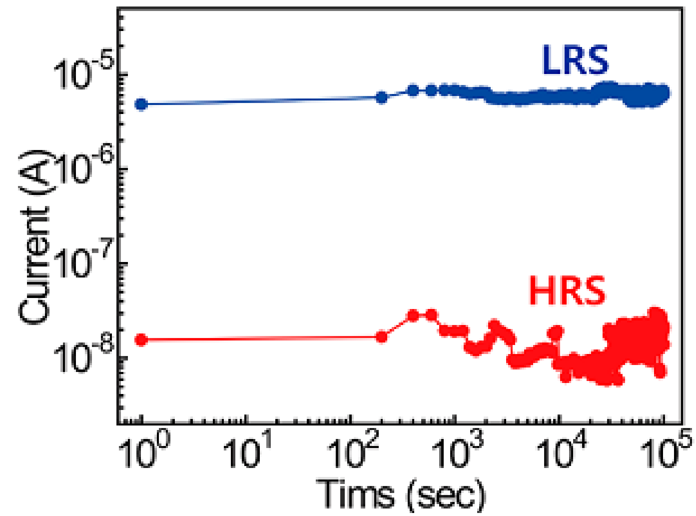
A novel organic resistive memory: progress beyond the state of the art



Best retention time in air reported so far in literature!

- **Retention time ~ $2.6 \cdot 10^7$ sec (<u>16 MONTHS</u>)**
- **Lifetime of 24 months (at the moment)**



Hwang et al., Nano Lett.2012, 12, 2217−222

So far…Maximum retention time <u>in air</u> in the order of 10^5 s (some days)

G. Casula et al., *Organic Electronics* 18, 17-23 (2015)