Outlines

- History of Conjugated Polymers
- Electronic Structures of Conjugated Polymers
- Polymer Light-emitting Diodes
- Polymer-based Thin Film Transistors
- Polymer-based Photovoltaics
- Polymers for Memory devices

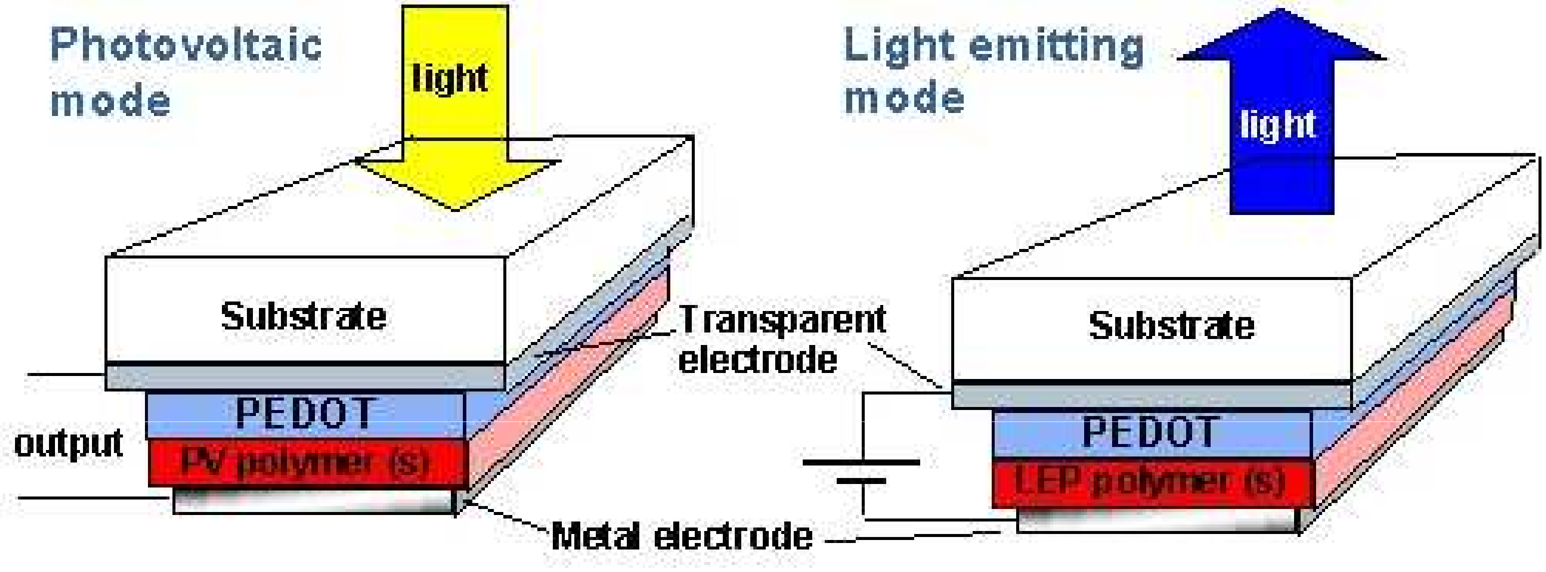
Reviews

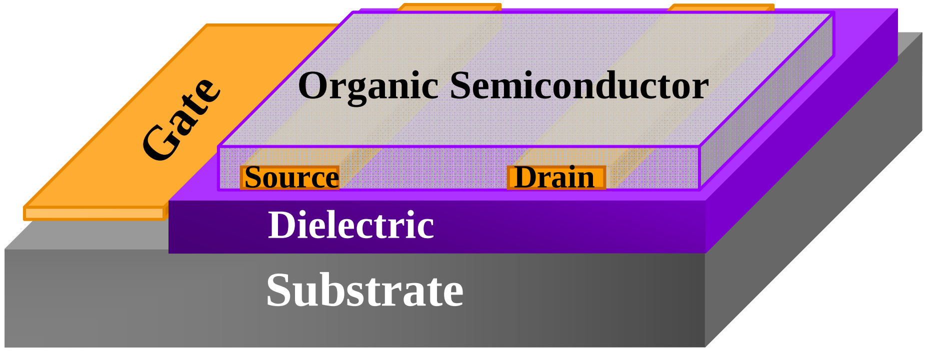
- E. T. Kang et al. *Prog Polym Sci* **2008**, *33*, 917.
- E. T. Kang et al. *Polymer* **2007**, *48*, 5182.
- E. T. Kang et al. *Encyclopedia of Nanoscience and nanotechnology* **2007**.
- Y. Yang et al. *Adv Mater* **2006**, *16*, 1001.
- J. C. Scott et al. *Adv Mater* **2007**, *19*, 1452.

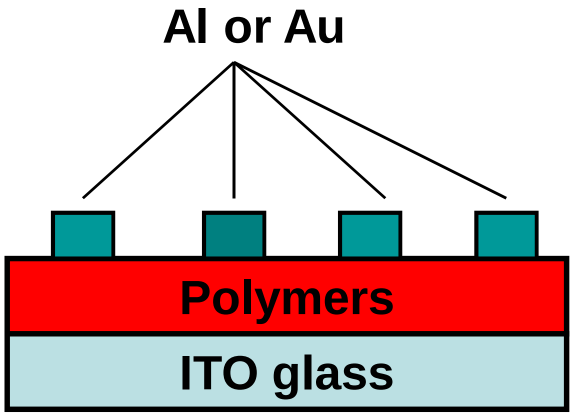
Device Applications of Donor-Acceptor Conjugated Polymers in My Group

Polymer Solar Cells

Polymer Light-emitting Diodes





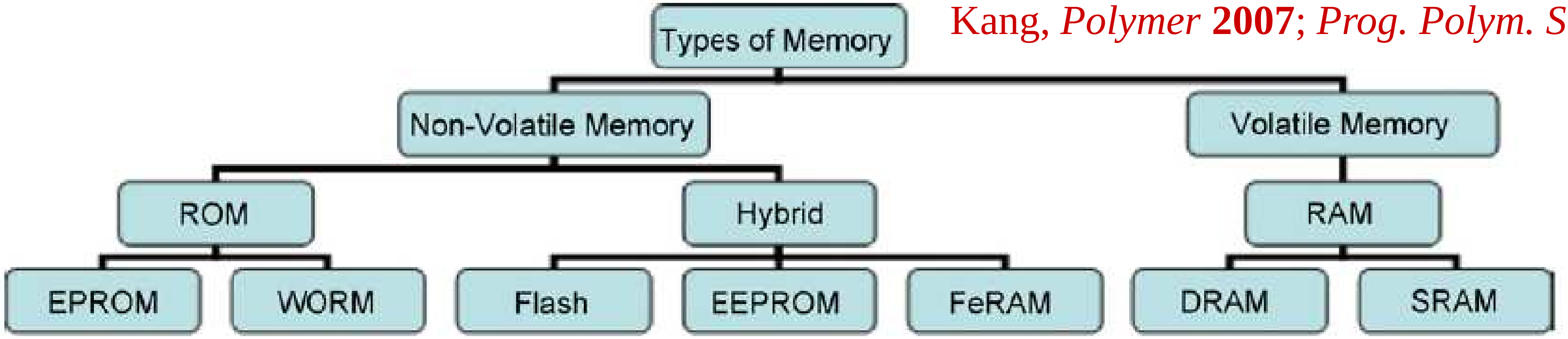


Polymer Thin Film Transistors

Polymer Memory Devices

Polymer Based Memory Devices

Kang, *Polymer* **2007**; *Prog. Polym. Sci.* **2008**

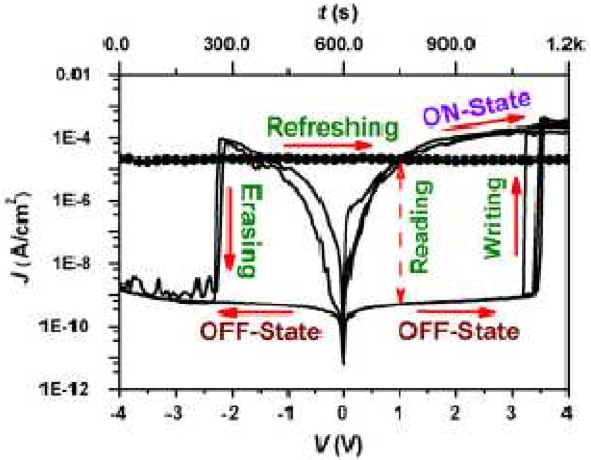


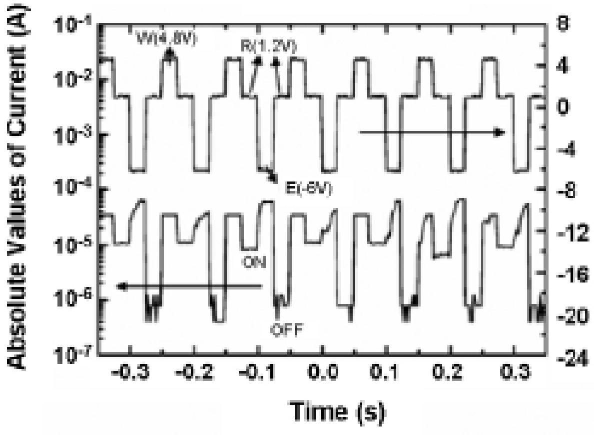
Types of Memory

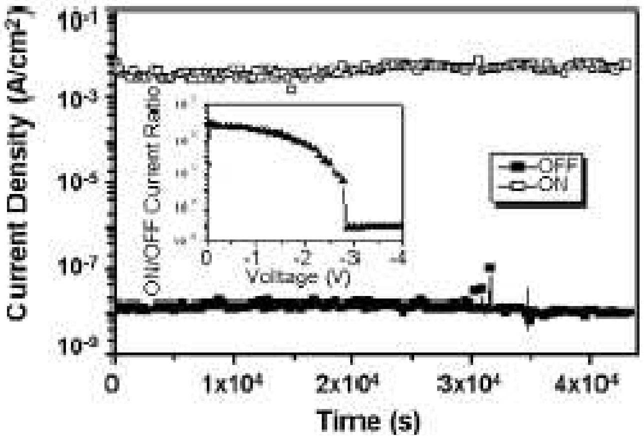
- Non-Volatile Memory
  - ROM
    - EPROM
    - WORM
  - Hybrid
    - Flash
    - EEPROM
    - FeRAM
- Volatile Memory
  - RAM
    - DRAM
    - SRAM

Basic Parameters

- **ON/OFF current ratio (higher value with minimal misreading error; >10^4)**
- **Switching (write or erase) time (~ms) and read time (~100 ns)**
- **Retention ability (> 1 day)**
- **Programmable (or WRER) cycles (>10^3 cycles)**
- **Long term stability under voltage stress or read pulse (>10^7 times)**



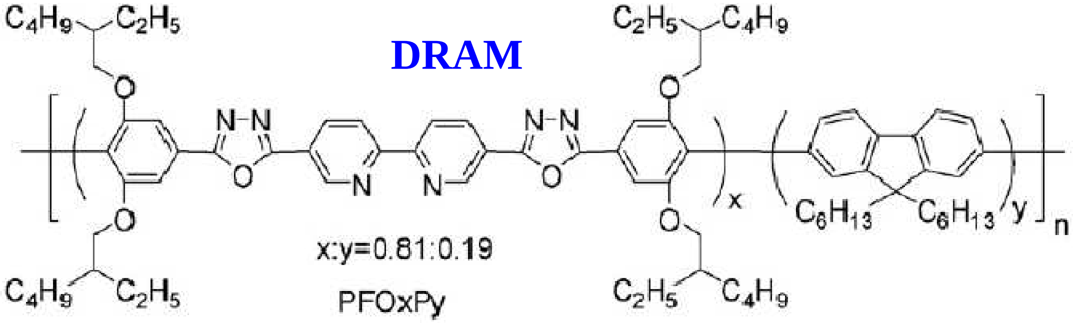




Polymer Based Memory Devices (Literature)

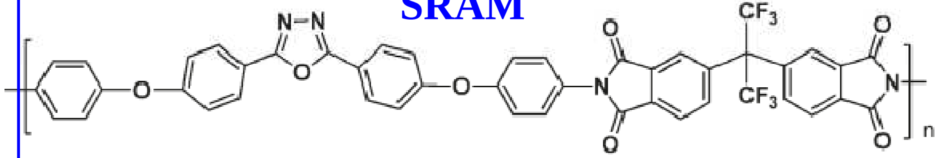
Volatile

DRAM



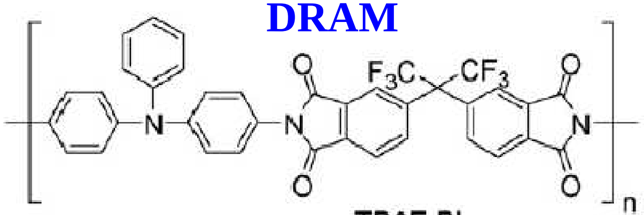
PFOxPy

SRAM



P(BPPO)-PI

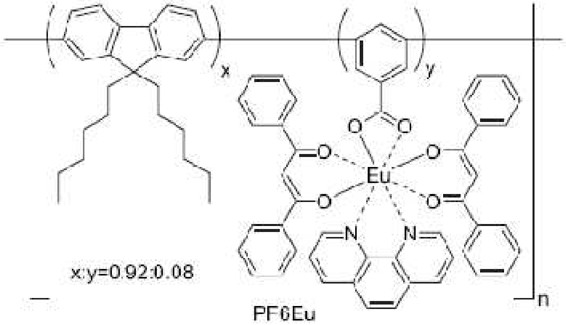
DRAM



TP6F-PI

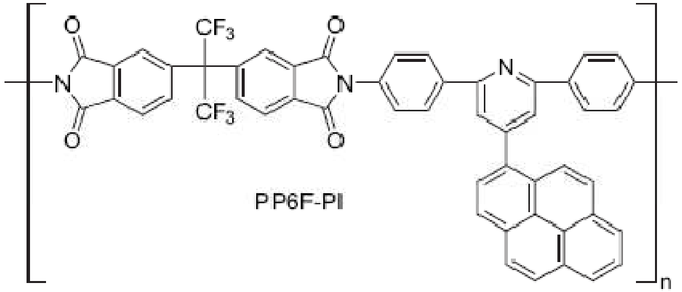
Non-Volatile

WORM



PF6Eu

Flash



PP6F-PI

Kang, Polymer **2007**, *33*, 917

Prog. Polym. Sci. **2008**, *33*, 917

Q: Could we develop thermally stable polymers for memory device applications?

Introduction to Computer Memory

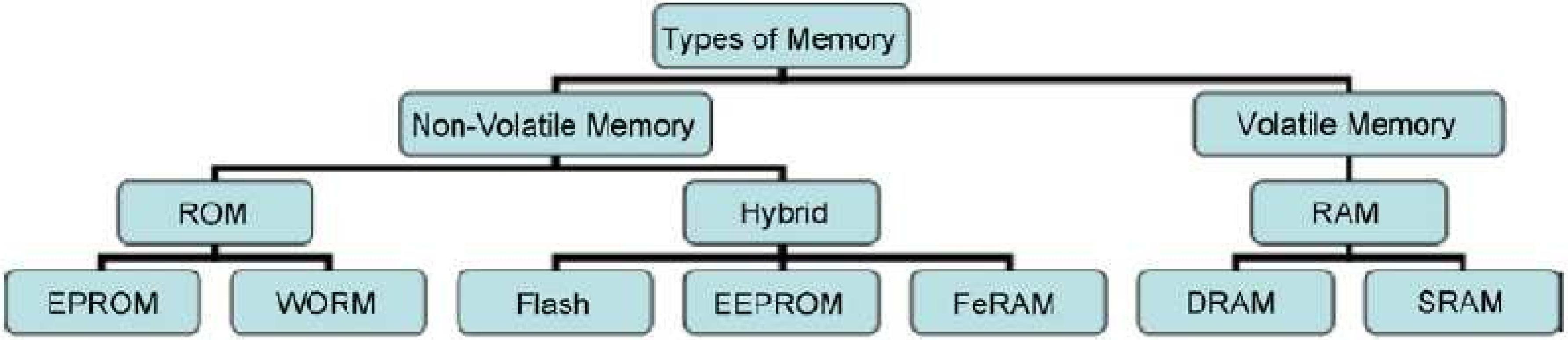
Computer memory refers to devices that are used to store data or programs (sequences of instructions) on a temporary or permanent basis for use in an electronic digital computer. Computers represent information in binary code, written as sequences of 0s and 1s. Each binary digit (or "bit") may be stored by any physical system that can be in either of two stable states, to represent 0 and 1. Such a system is called bistable. This could be an on-off switch, an electrical capacitor that can store or lose a charge, a magnet with its polarity up or down, or a surface that can have a pit or not. Computer memory is usually referred to the semiconductor technology that is used to store information in electronic devices. There are two main types of memory: Volatile and Non-volatile.

An electronic memory is fast in response and compact in size, and can be Connected to a central processing unit.

Volatile memory: lose the stored data as soon as the system is turned off. It requires a constant power supply to retain the stored information.

Non-volatile memory: retain the stored information even when the electrical power has been turned off.

Classification of Electronic Memories



ROM (**R**ead-**O**nly **M**emory)

WROM (**W**rite-**O**nce **R**ead-**M**any **T**imes): CD-R or DVD±R

EPROM (**E**rasable **P**rogrammable **R**ead-**O**nly **M**emory)

EEPROM (**E**lectrically **E**rasable **P**rogrammable **R**ead-**O**nly **M**emory)

FeRAM (**F**erroelectric **R**andom **A**ccess **M**emory)

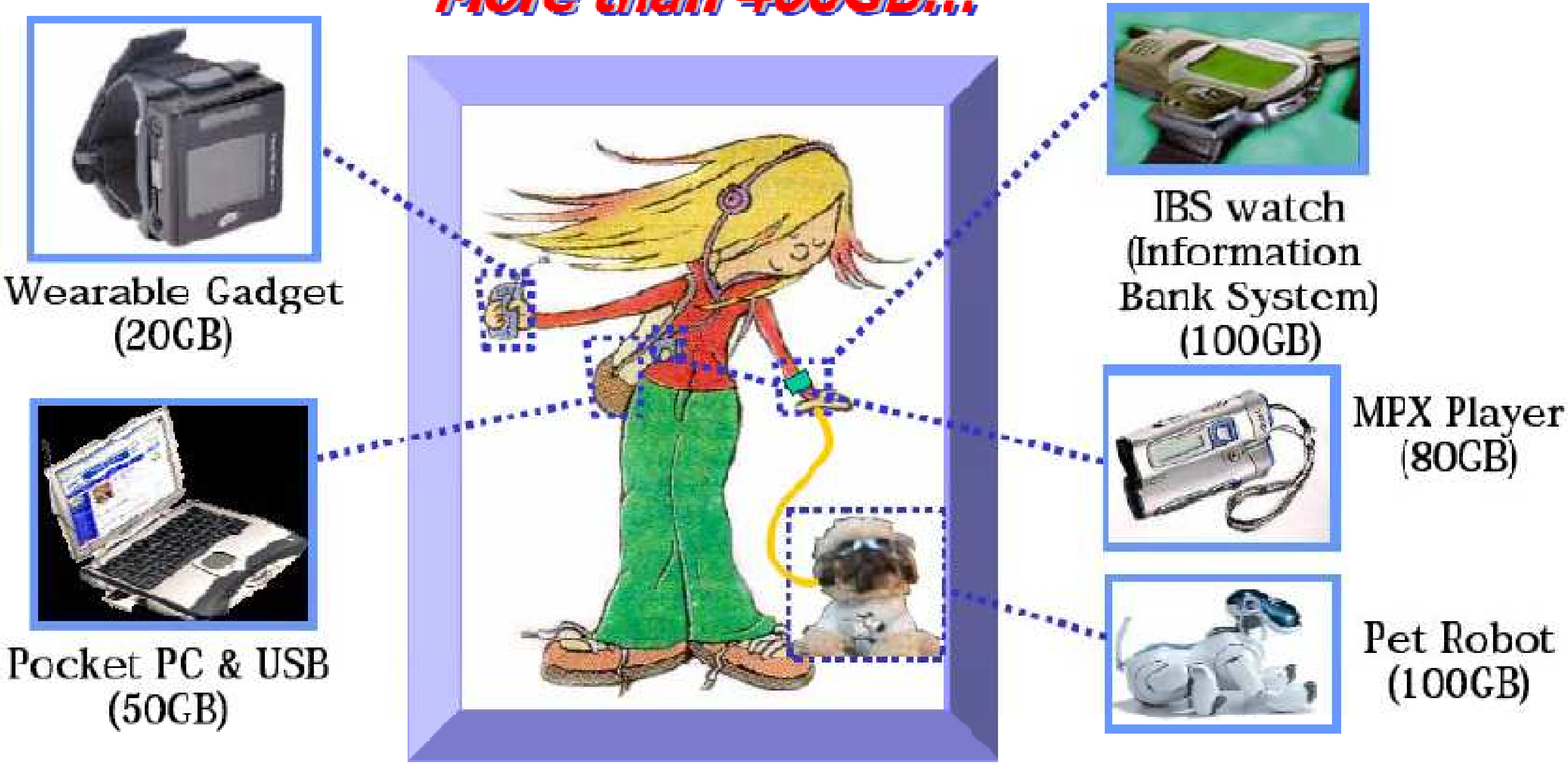
Flash: DPA, mobile PC, video player and digital camera

DRAM (**D**ynamic **R**andom **A**ccess **M**emory): As real capacitors have a tendency to leak electrons, the information eventually fades unless the capacitor charge is refreshed periodically.

SRAM (**S**tatic **R**andom **A**ccess **M**emory): it does not need to be periodically refreshed, as SRAM uses bistable latching circuitry to store each bit.

Memory in Your Hands (~2010)

More than 400GB...



Phone, Data, Game, GPS, Entertainment….

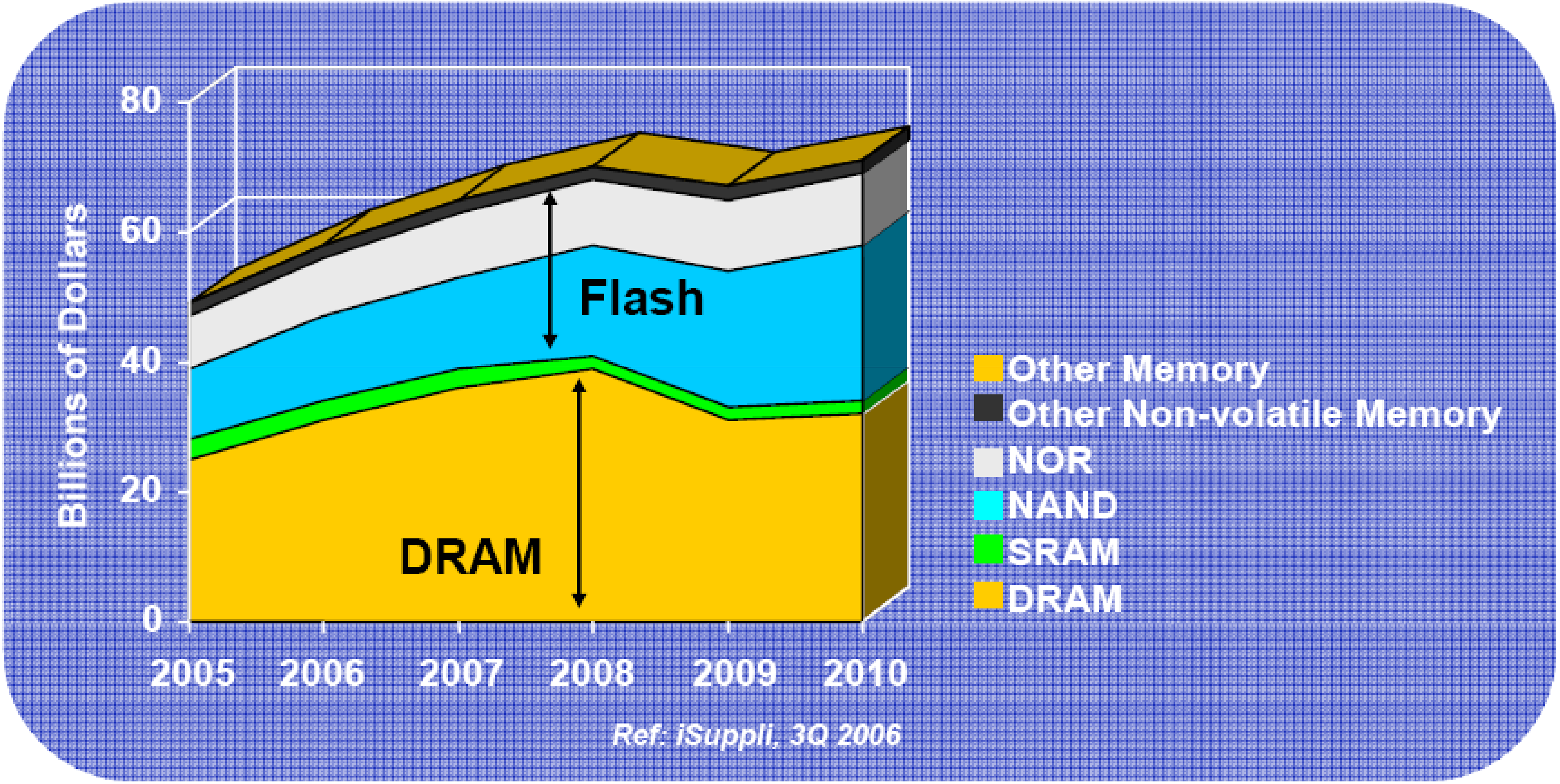
C. Kim, *“Future Memory Technology: Trends and Challenges”* ISQED **(2005)**

Applications of Memory

- The identification in RFID
  - Track and trace
- Sensors
  - Recording temperature, humidity, etc. History of a product
- E-paper displays
  - Look-up tables for previous states of pixels
- Game, transit and collectible customer etc. cards
  - Store points, number of trips etc.
- More bits = more information
  - Some applications as little as 15 bits, other need kbit, Mbit, Gbit
- Overall the trend is to more memory devices

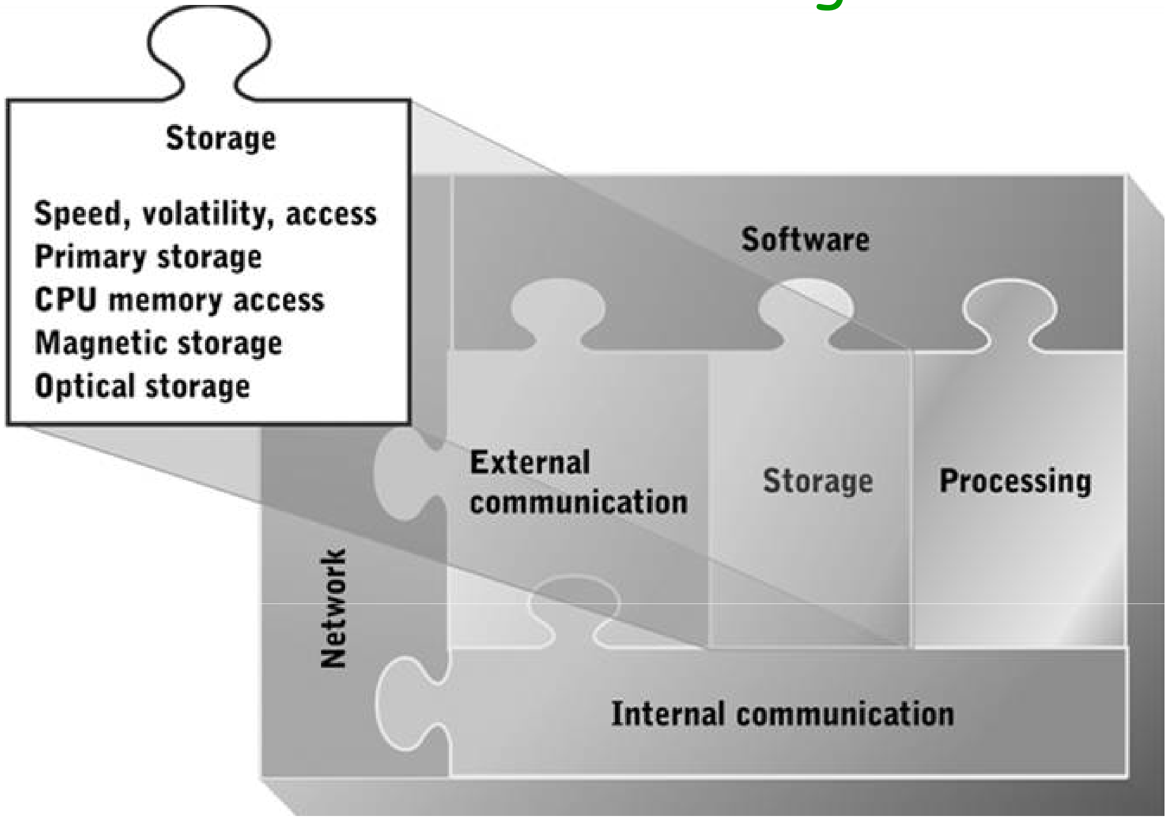
Memory Market

DRAM and flash dominate



Source: Gary Bronner (Rambus), Stanford EE 309 lecture, Fall 2007.

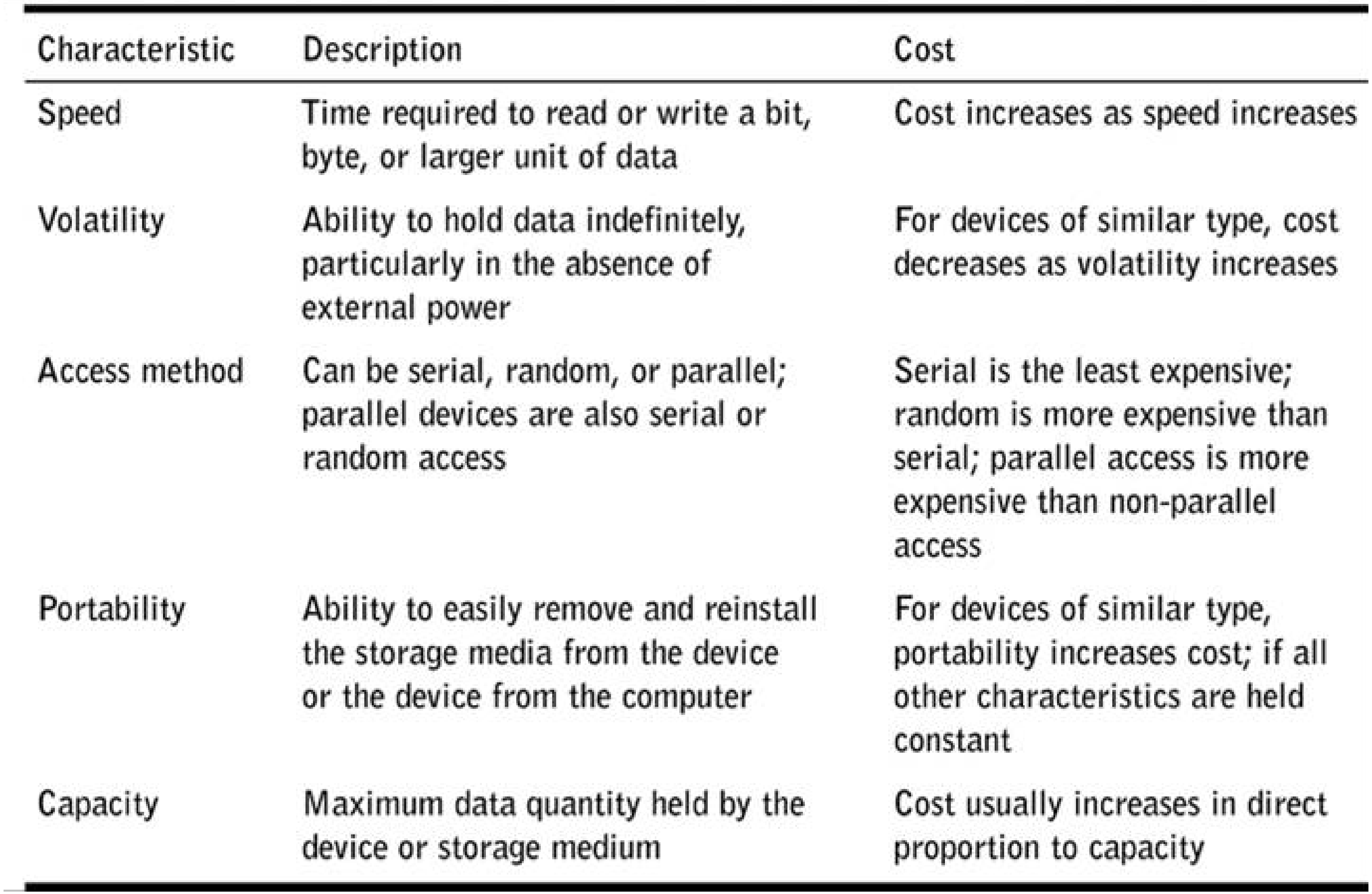
Introduction to Data Storage Technology



- Consist of a read/write mechanism and a storage medium
  - Device controller provides interface
- Primary storage devices
  - Support immediate execution of programs
- Secondary storage devices
  - Provide long-term storage of programs and data

Introduction to Data Storage Technology

Characteristic of storage device



Characteristic	Description	Cost
Speed	Time required to read or write a bit, byte, or larger unit of data	Cost increases as speed increases
Volatility	Ability to hold data indefinitely, particularly in the absence of external power	For devices of similar type, cost decreases as volatility increases
Access method	Can be serial, random, or parallel; parallel devices are also serial or random access	Serial is the least expensive; random is more expensive than serial; parallel access is more expensive than non-parallel access
Portability	Ability to easily remove and reinstall the storage media from the device or the device from the computer	For devices of similar type, portability increases cost; if all other characteristics are held constant
Capacity	Maximum data quantity held by the device or storage medium	Cost usually increases in direct proportion to capacity

Advantage of Organic/ Polymer Memory Devices

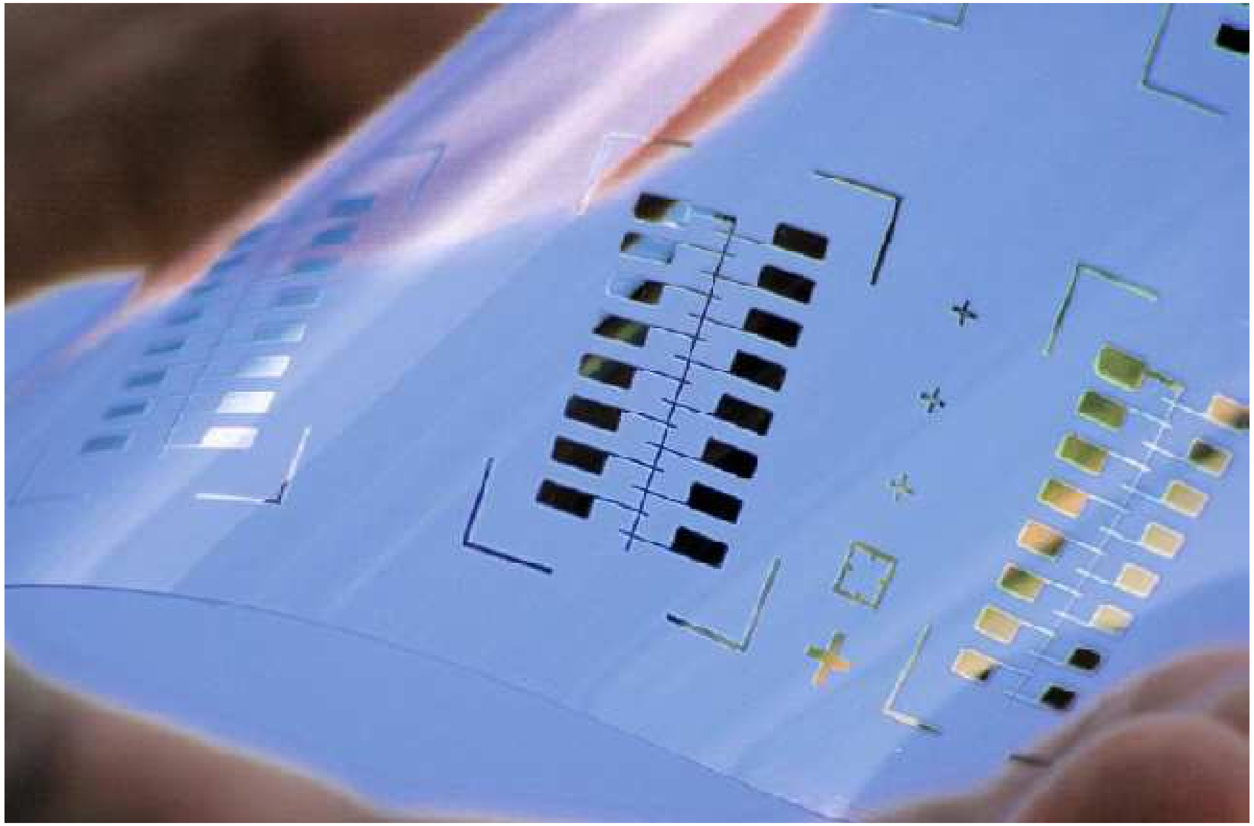
- -molecular scale memory applications with good processibility, miniaturized dimensions and the possibility for molecular design through chemical synthesis.

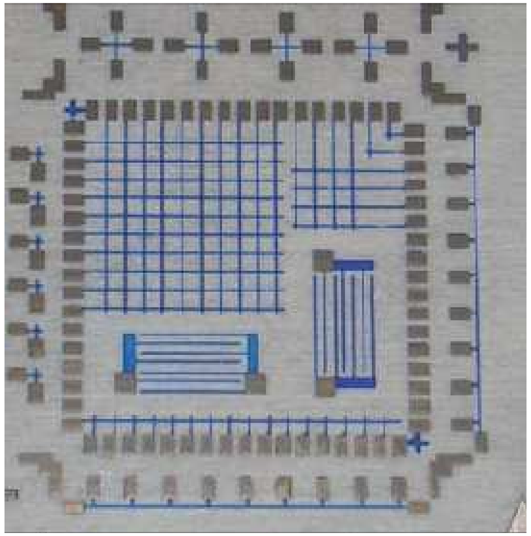
- -simplicity in device structure, good scalability, low cost, potential, low power operation, multiple state properties. 3D stacking capability, and large capacity for data storage.

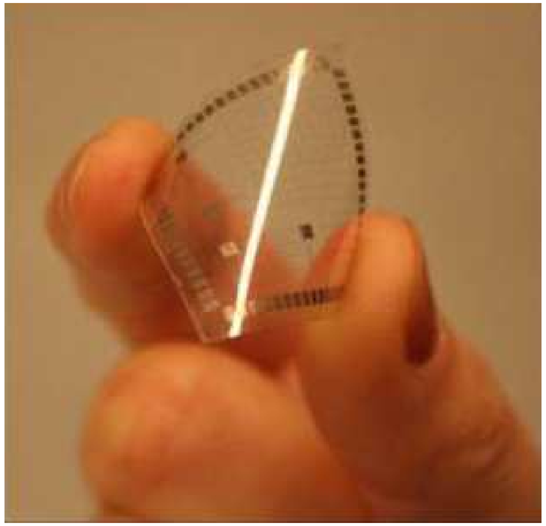
- -Good mechanical properties, and design flexibility

- -Could be an alternative or supplementary technology to the conventional memory technology in the micro/nanoscale.

Fully Printed Passive Array Memories







By Thin Film Electronics

Organic Memory Devices

Adv Mater **2007**, *19*, 1452

Small Molecules

Switching type	Structure
1. Hysteresis, without threshold or NDR	ITO / NiPc:PAH / Al
2. Reverse polarity switching, no NDR	Au / anthracene-*co*-PMMA / Al
	ITO / DDQ, TAPA, Fluorescein, Eosin Y or Rose Bengal : PAH / Al
3. Threshold, but volatile	Al / tetracene / Au
	Ag / anthracene / Ag
	Al / pentacene / Al
4. WORM	ITO, Au, or Al / Alq3 / Al
5. Switching by either polarity, NDR	ITO or Au / Alq3 or NPB / Al, Ag or Au
	Al / AIDCN / Ag

Polymer

Switching type	Structure
1. Hysteresis, without threshold or NDR	ITO / P6OMe / Al
2. Reverse polarity switching, no NDR	Al / PSF / Ba:Al
3 Volatile or 4 WORM depending on conditions	ITO or Mo / PMMA, PS, PEMA or PBMA / graphite
5. Switching by either polarity, NDR	ITO / MEH-PPV / Al

Mobile Ion

Switching type	Structure
1. Hysteresis, without threshold or NDR	PEDOT:PSS:NaCl / 6T-co-PEO / Al
2. Reverse polarity switching, no NDR	Pt / MEHPPV / RbAg5I4 /Ag
	? / PPhA:NaCl / ?

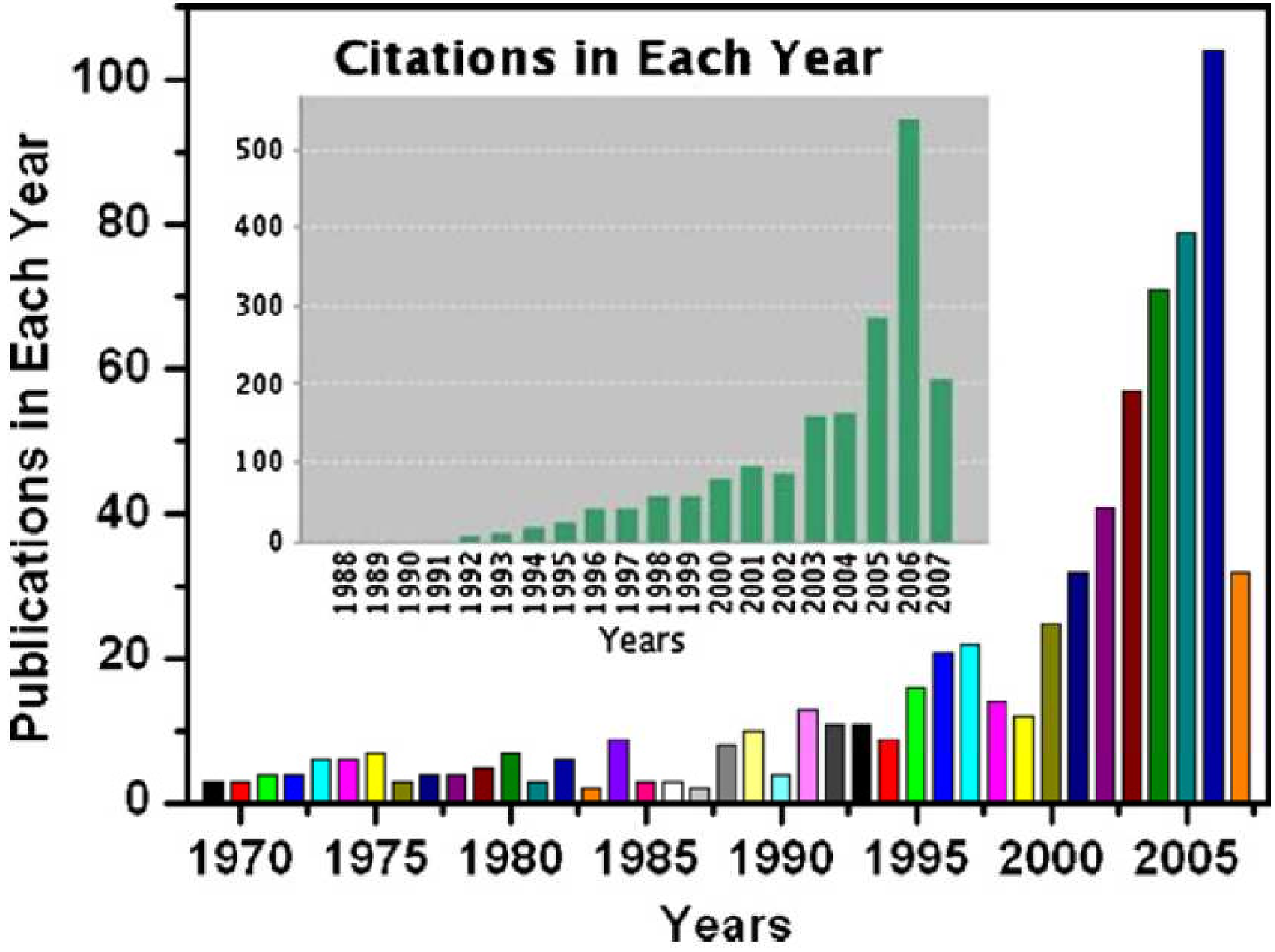
D-A Complex

Switching type	Structure
2. Reverse polarity switching, no NDR	Cu / CuTCNQ / Al
	ITO / EuVB-co-PVK / Al
	ITO / PEDOT:PSS / RE-complex:PVK / LiF / Ca /Ag
	HOPG / NBMN:pDA / STM
	Al / CuTCNQ / Al
	Al / TTF:PCBM:PS
	HOPG / CDHAB / STM-W
	Cu / CuTCNQ / Cu
	ITO / P3HT:CNT / Al
3 or 4 Volatile or WORM depending on conditions	Cu / CuTCNQ / Al
4. WORM	Ag / DC:BDCP / Ag
	ITO / EuVB-co-PF / Al

Nanoparticle Blend

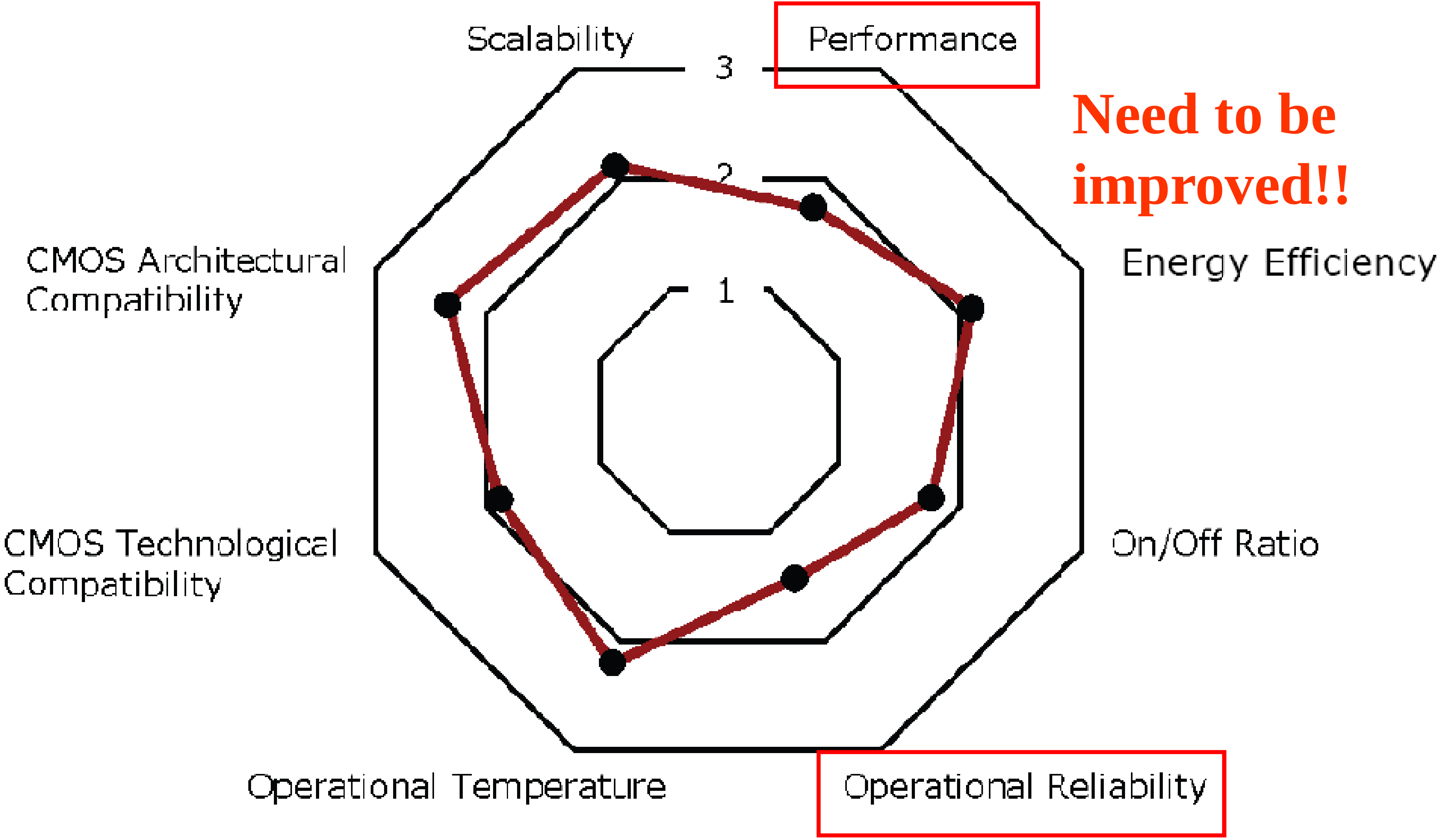
Switching type	Structure
1. Hysteresis, without threshold or NDR	Al / (Au-2NT or BET):PS / Al
2. Reverse polarity switching, no NDR	Al / AIDCN / (Al) / AIDCN / Al
	Al / (Au-DT):8HQ, or DMA:PS / Al
3. Threshold, but volatile	Al / (Au):PTFE / Au
	Pt / (Ag):gd-HMDS or gd-benzene / Pt
	Al / AIDCN / (Al):AIDCN / AIDCN / Al
	Ag / CNPF / (Ag) / CNPF / Ag
4. WORM	? / TDCN / (Ag) / TDCN / ?
5. Switching by either polarity, NDR	Al / Alq3 / (Al) / Alq3 / Al
	ITO / (Au-TPP):xBP9F / Al
	ITO / (Au-TPP):xHTPA / Ca / Al
	ITO / (Au-TPP):xHTPA / Al
	ITO / (Au-TPP):xHTPA / xHTPA / Al
	Al / NPB / (Al) / NPB / Al
	Cr / Alq3 / (Al) / Alq3 / Al
	Cu / Alq3 / (Al) / Alq3 / Al
	ITOI / Alq3 / (Al) / Alq3 / Al
	Au / Alq3 / (Al) / Alq3 / Al
	Ni / Alq3 / (Al) / Alq3 / Al l
	Al / Alq3 / (Mg) / Alq3 / Al
	Al / Alq3 / (Ag) / Alq3 / Al
	Al / Alq3 / (Cr) / Alq3 / Al
	Al / Alq3 / (CuPc) / Alq3 / Al
	Al / (Au-DT):P3HT / Al

Statistics of Publications and Citations on Organic and Polymer Memory Device



From ISI Web of Science, Engineering Village, ScienceDirect, SciFinder Scholar

Technology Performance Evaluation for Polymer Memory



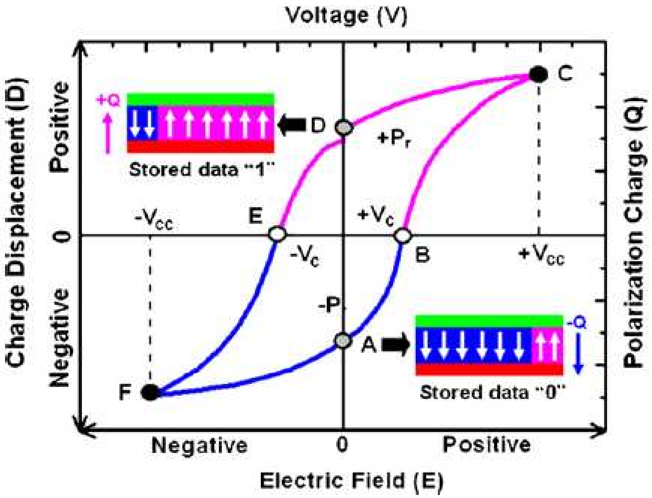
Need to be improved!!

The ITRS has identified polymer memory as an emerging memory technology since year 2005.

International Technology Roadmap for Semiconductor **2007**

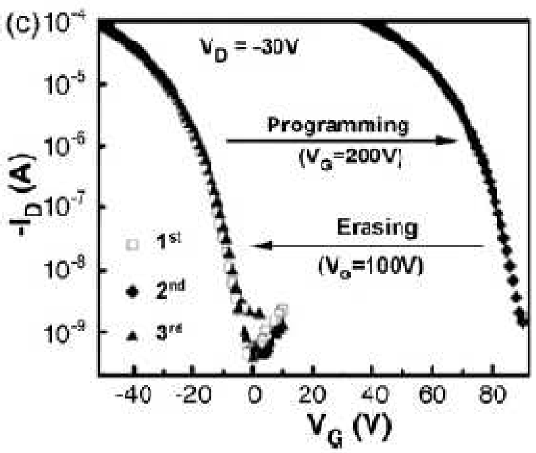
Introduction to Memory Devices

Capacitor-type



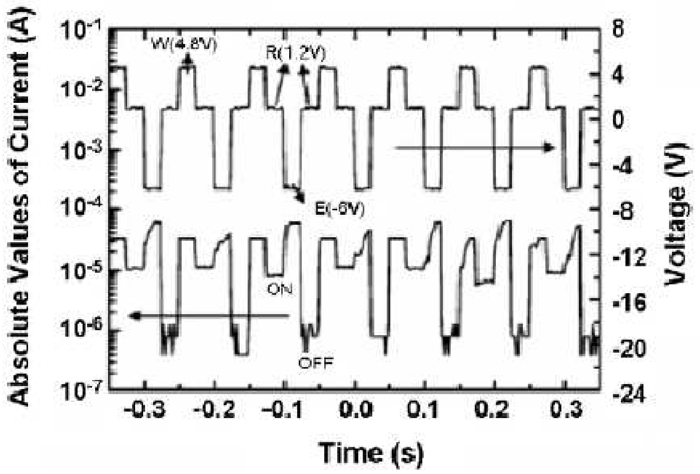
The capacitor stores charges, of opposite sign, on two parallel plate electrodes. Each bit of data is stored in a separated capacitor

Transistor-type



Charge storage and polarization in the dielectric layer or interface of an OTFTs

Resistor-type



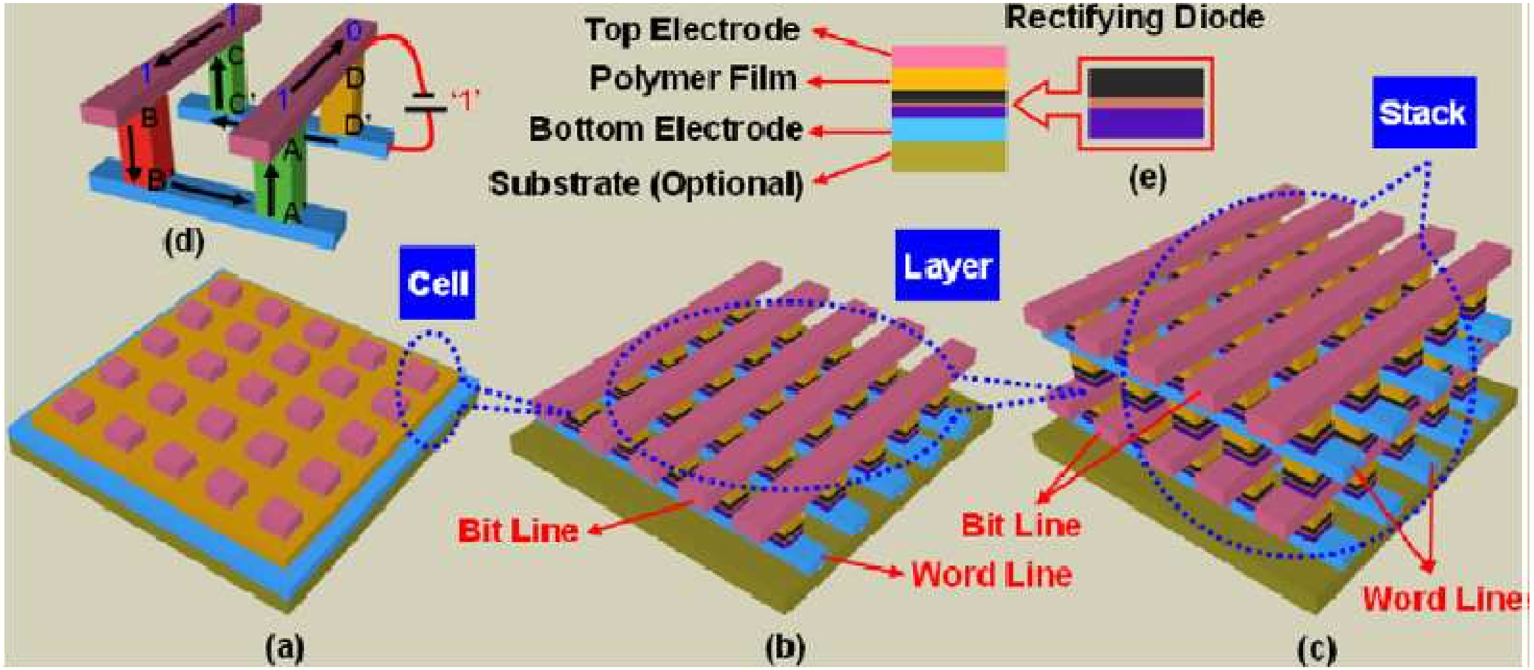
Data storage is based on the high and low conductivity states (electrical bistability) of resistor in response to the applied electric filed

Performance factors of RRAM: filamentary conduction, space charges and traps, charge transfer effects, conformation changes, polymer fuse effects, ionic conduction., tunneling.

Fundamentals of Resistor-type Memory

Resistance change memory stores data based on the electric stability (ON and OFF states) of materials arising from changes in certain properties such as charge transfer, filament formation, and tapping-detrapping effect in response to the applied electric field.

General Device Structures



(a) 5x5 testing cell (MIM on supporting substrate) (b) 5(word line)x5(bit line) cross-point memory (c) 2(stacked layer)x5(word line)x5(bit line) (d) parasitic paths in cross-point memory (e) rectifying diode integrated to avoid parasite current

Physics of Resistivity Switching

- **For a memory device that relies on a change in the resistivity of the memory cell, the resistance of the materials changed by an electric input is of fundamental requirement.**
- **This generally involves a change in the properties of the material in response to and electrical input.**
- **Actually the physics of resistivity switching for many newly discovered memory devices is not clearly known and largely debated.**
- **Often the application of a voltage or a current will induce resistivity switching and the proposal of mechanism need to be very careful when interpreting results or claim.**

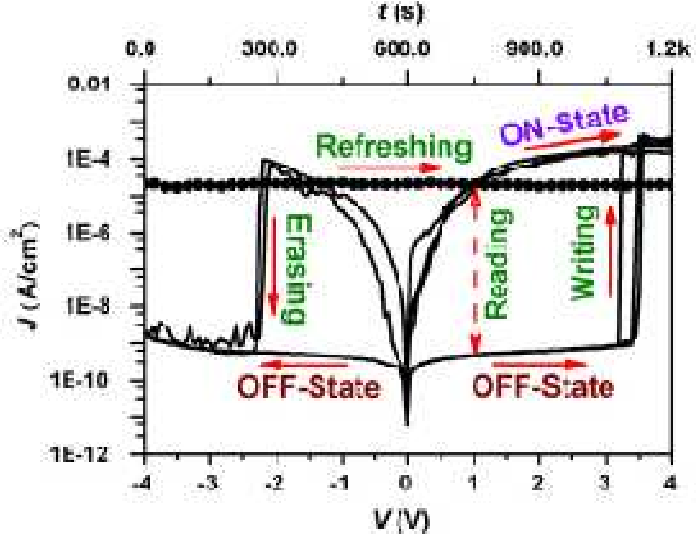
Basic electric characteristics of Resistor-type Memory

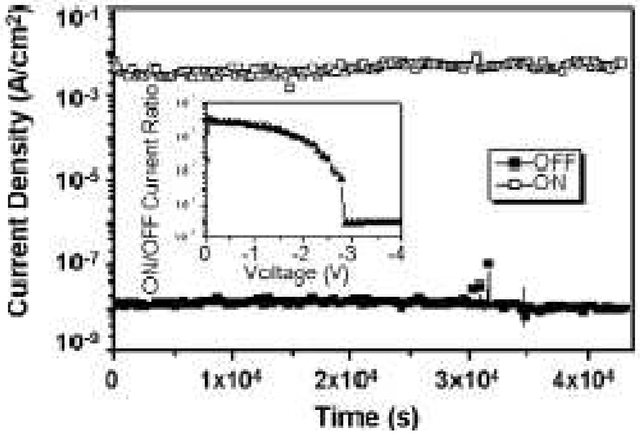
Application of a sufficient electric field to an insulator can eventually lead to a deviation from linearity in the resultant current response including (i) threshold switching (ii) memory switching (iii) electrical hysteresis (iv) rectifying (v) negative differential resistance (NDR)

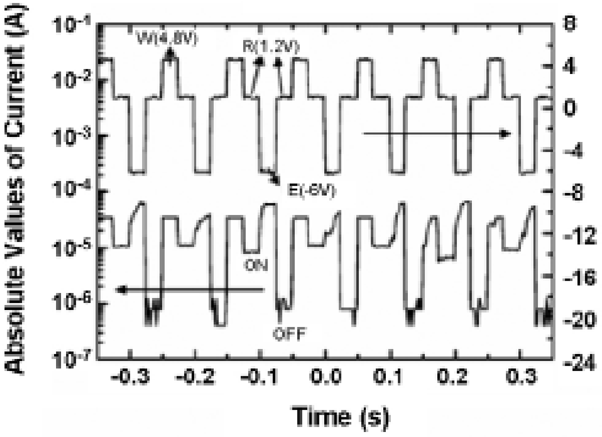
(ii) & (iii) have bistability in a voltage or current range

Basic Parameters

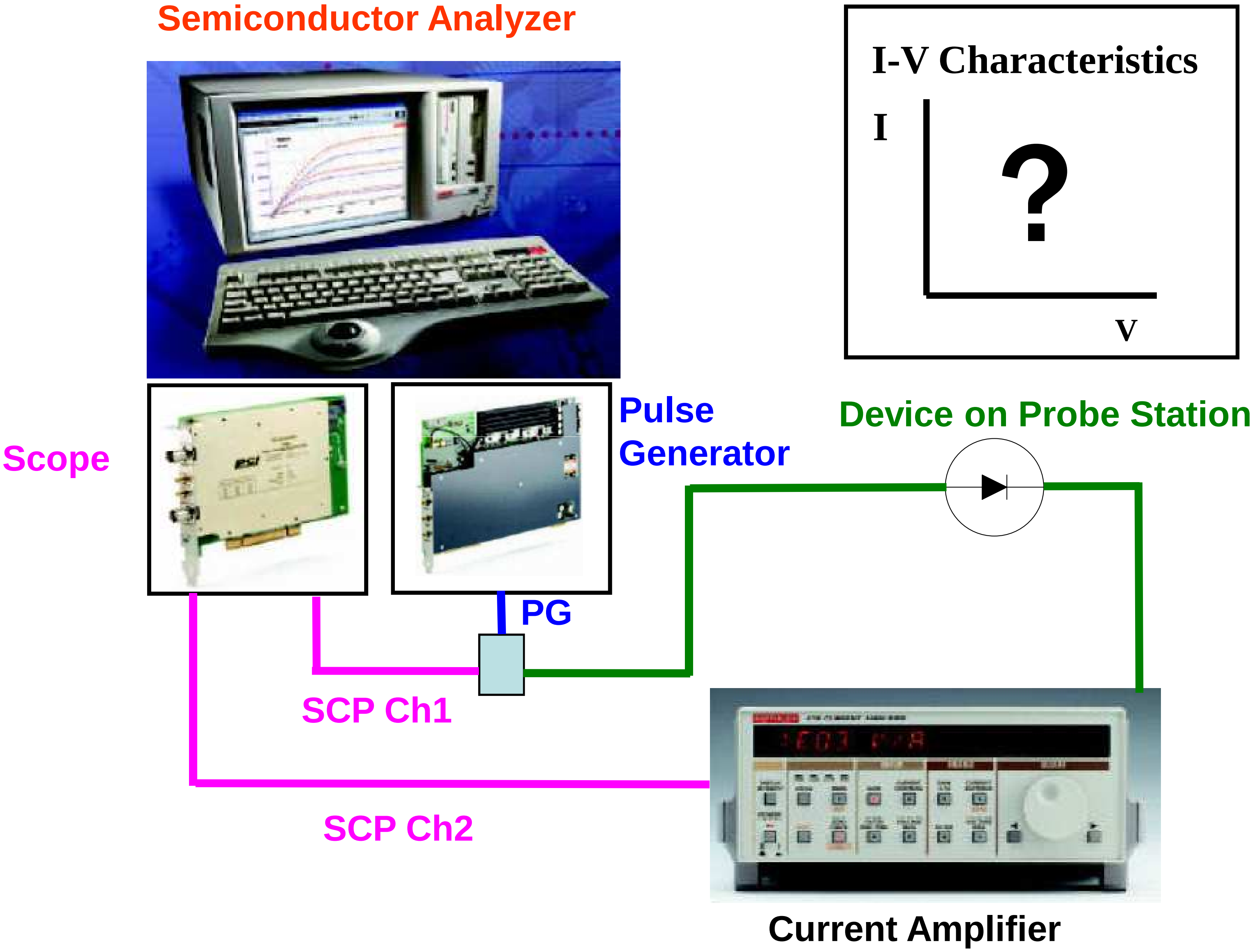
- ON/OFF current ratio
- Switching (write or erase) time and read time
- Retention ability for non-volatile memory
- Programmable (or WRER) cycles
- Long term stability under voltage stress or read pulse
- Power consumption and cost







Measurements of the Memory Device



Semiconductor Analyzer

I-V Characteristics

I

?

V

Scope

Pulse Generator

Device on Probe Station

PG

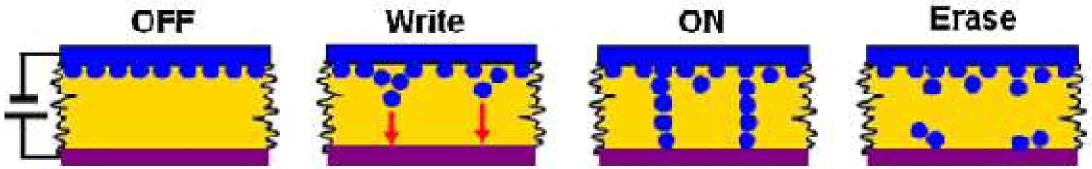
SCP Ch1

SCP Ch2

Current Amplifier

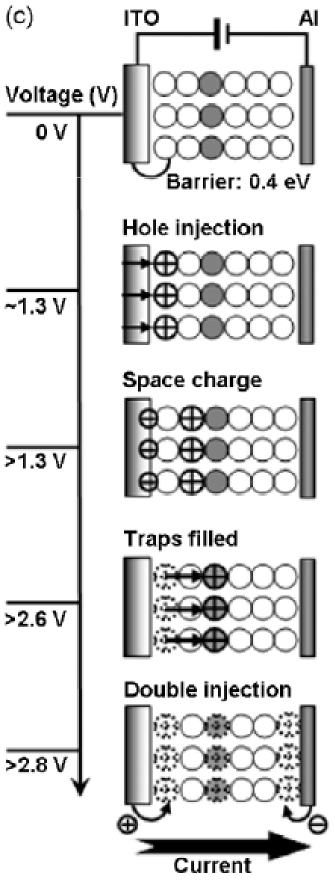
Mechanism of Resistor-type Memory

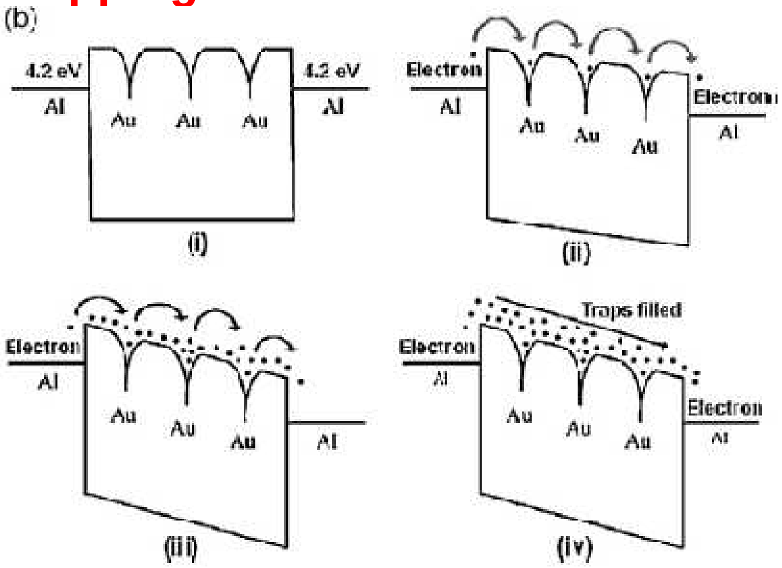
Filamentary conduction



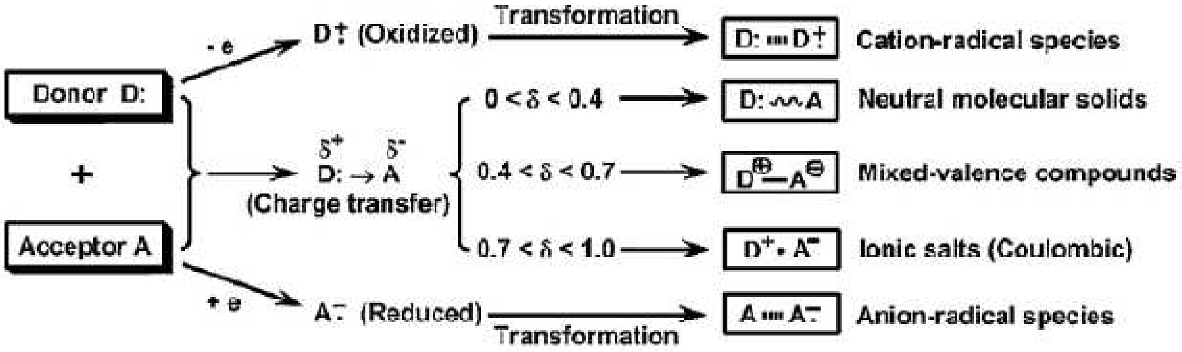
Metallic filament resulting from local fusing, migrating or sputtering electrode trough the film

Trapping & De-trapping





Charge Transfer (CT) Effect



Filament Conduction Mechanisms

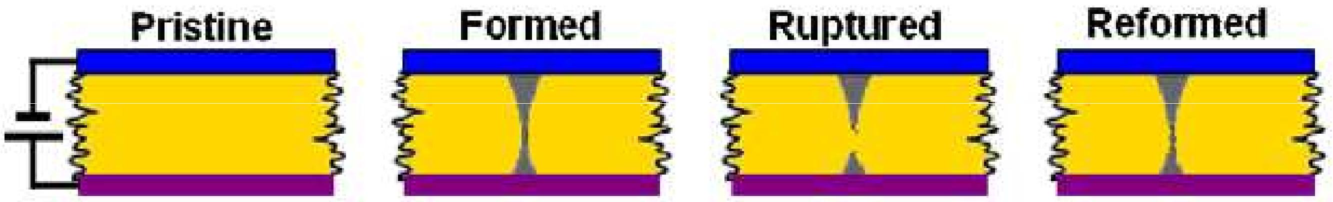
- In general, when the **on state current is highly localized to a small fraction of the device area**, the phenomenon is termed as "filamentary" conduction.

Resistor-type Memory: Filamentary Conduction Mechanisms

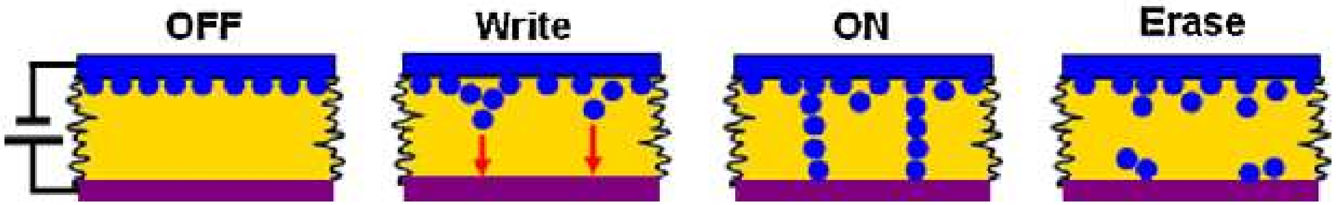
If filaments are formed in a device, (i) the ON state current will exhibit metallic I-V characteristics and will increase as the temperature is decreased and (ii) the injection current will be insensitive to device area or show a random dependence because the dimension is much smaller when compare to the device area.

Filament formation and switching effect

(a) Carbon-rich filaments



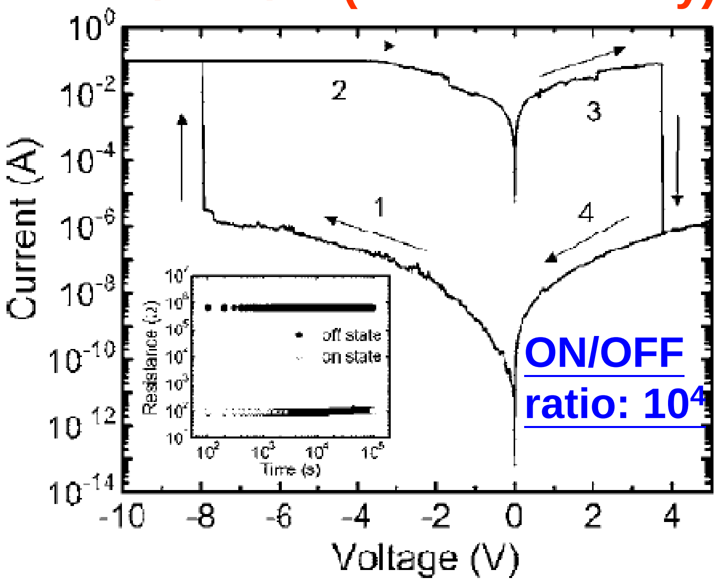
(b) Metallic filaments



The filament occurrence depends on three parameters: electrode thickness, film thickness, and the nature of the forming atmosphere.

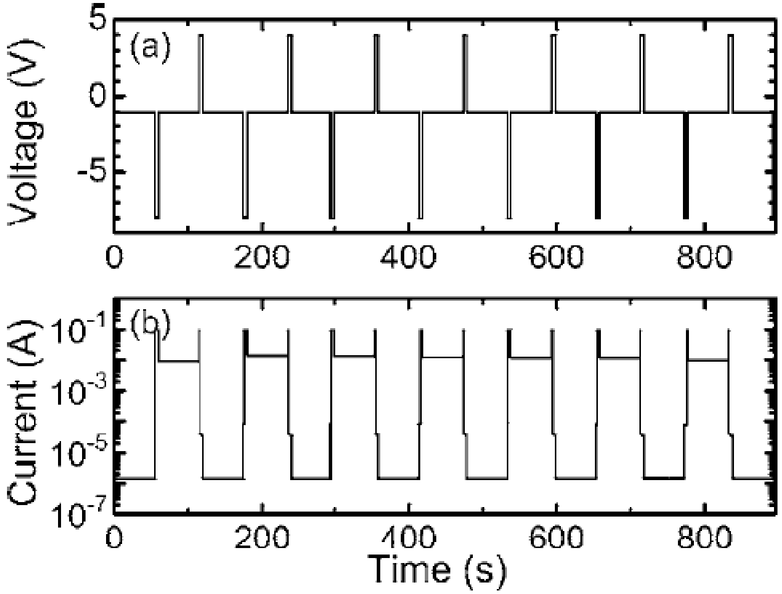
Resistor-type Memory: Filamentary Conduction Mechanisms

Al/PVK/Al (filament theory)

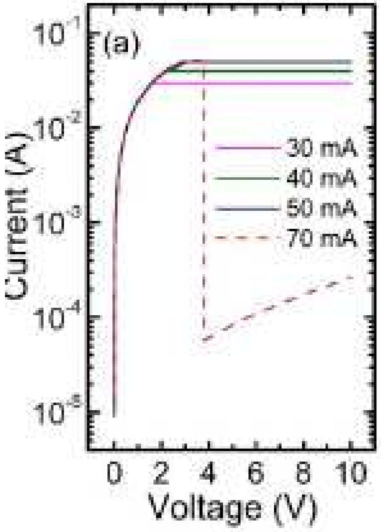


ON/OFF ratio: 10^4

WRER cycles



Turn ON compliance 50 mA



Switch-OFF is triggered by current

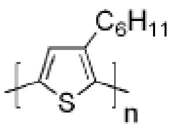
The ON state resistance can be controlled by restricting the ON state current which will influence the turn OFF current.

The mechanism is explained on the basis of the filament theory.

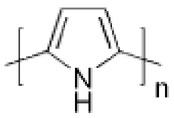
Appl Phys Lett **2005**, *87*, 122101

Resistor-type Memory: Filamentary Conduction Mechanisms

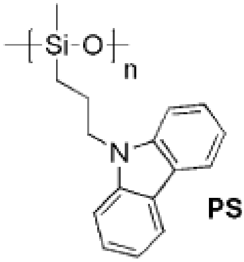
The presence of strong coordinating heteroatom (S or N) with metal ions and π-conjugation show reproducible filament formation behavior.



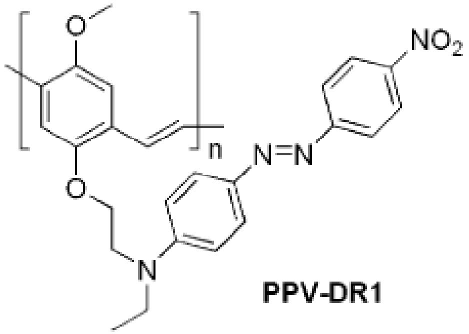
P3HT



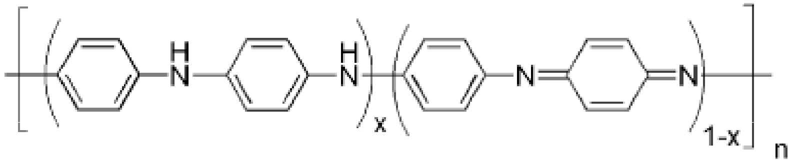
Polypyrrole



PSX-Cz



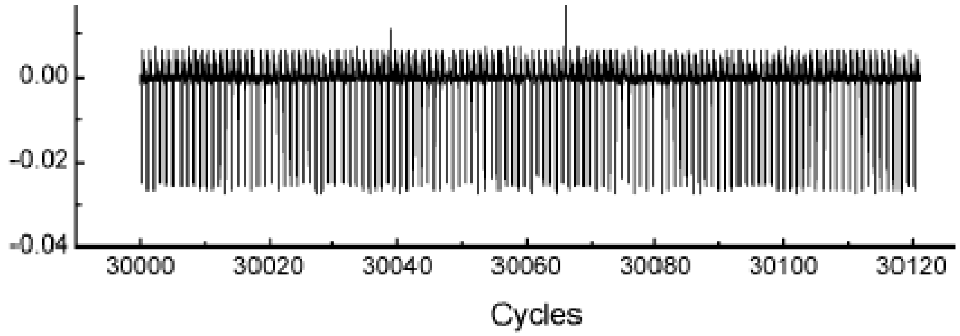
PPV-DR1

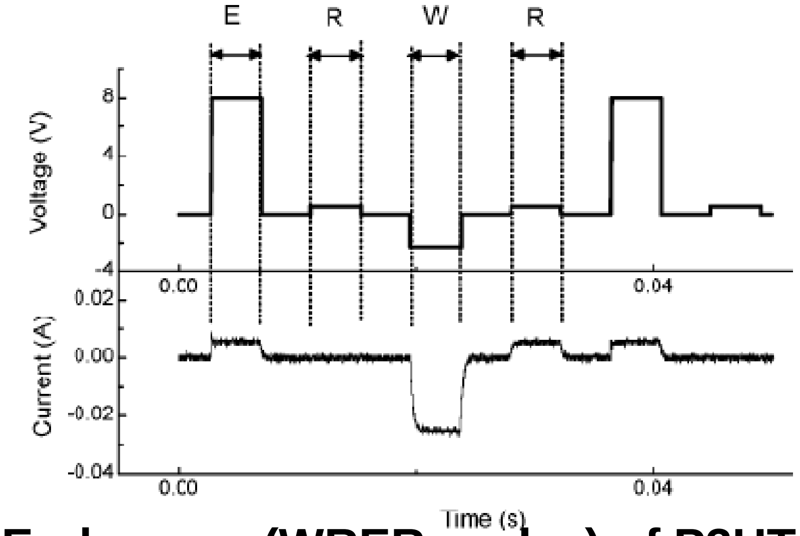


Polyaniline

nm-sized metal bridge connects between the electrodes

Perfect switch endurance until $3x10^4$ cycles



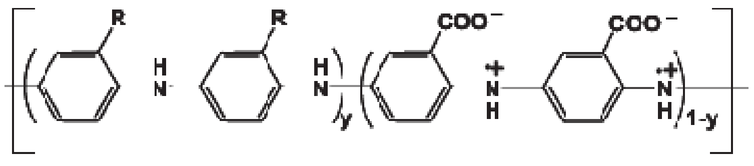


Endurance (WRER cycles) of P3HTdevice

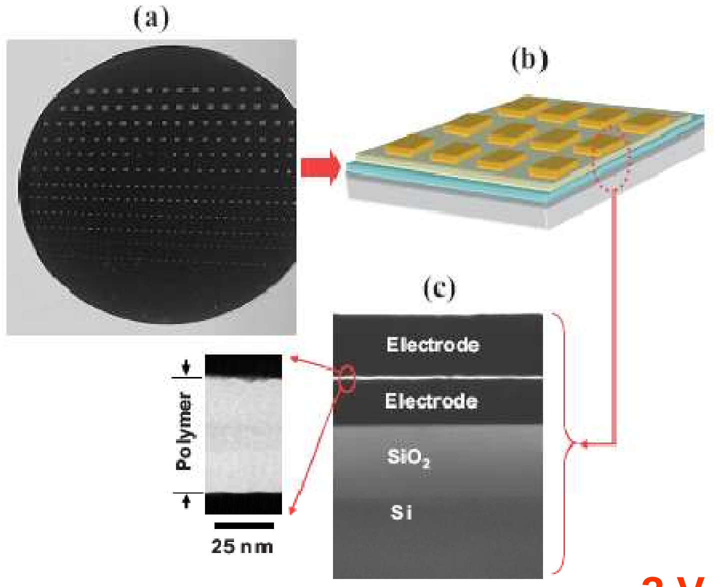
J Phys Chem B **2006**, *110*, 23812

Resistor-type Memory: Filamentary Conduction Mechanisms

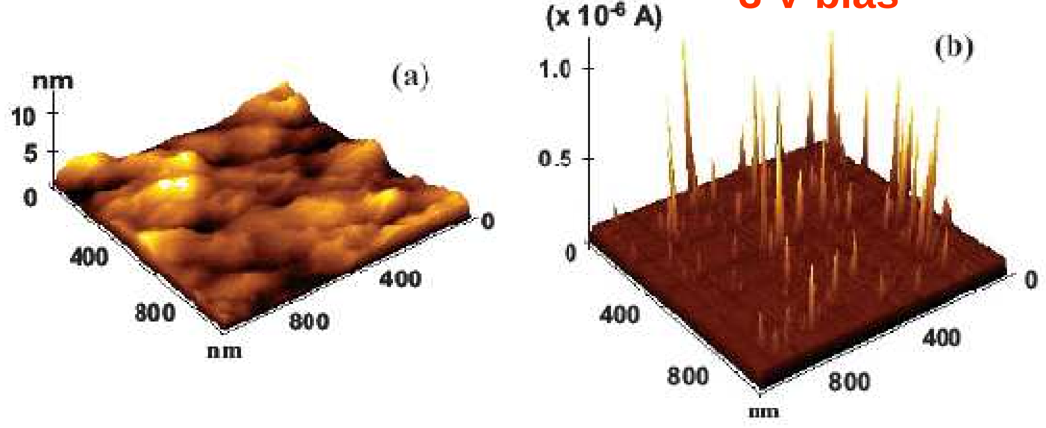
Doping-PANI semiconducting polymers



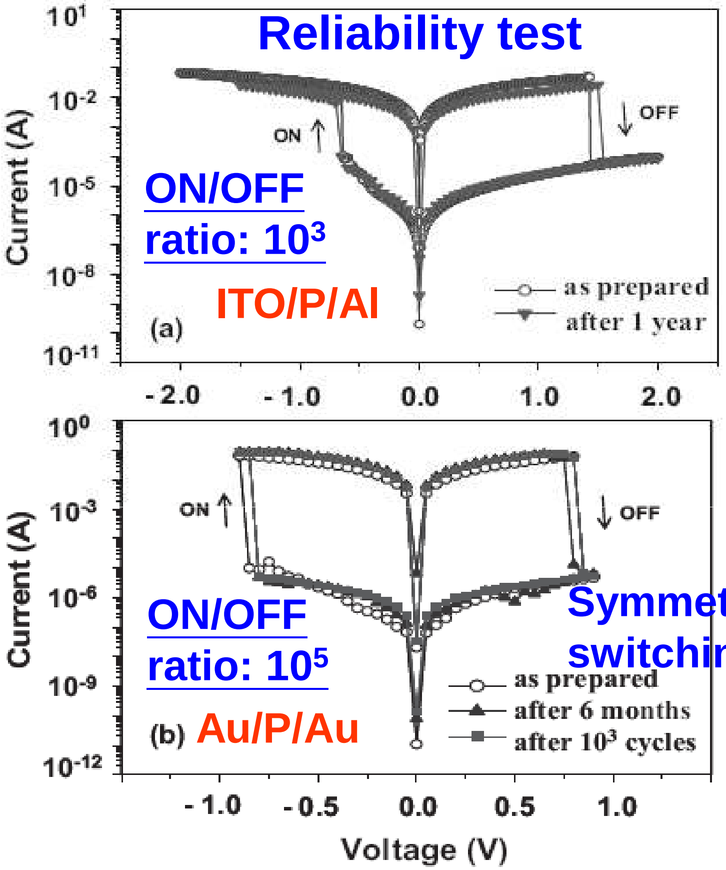
Self-doped PANI-PARA



-3 V bias



Fast switching response ~ 80 ns



Reliability test

ON/OFF ratio: 10^3

ITO/P/Al

ON/OFF ratio: 10^5

Au/P/Au

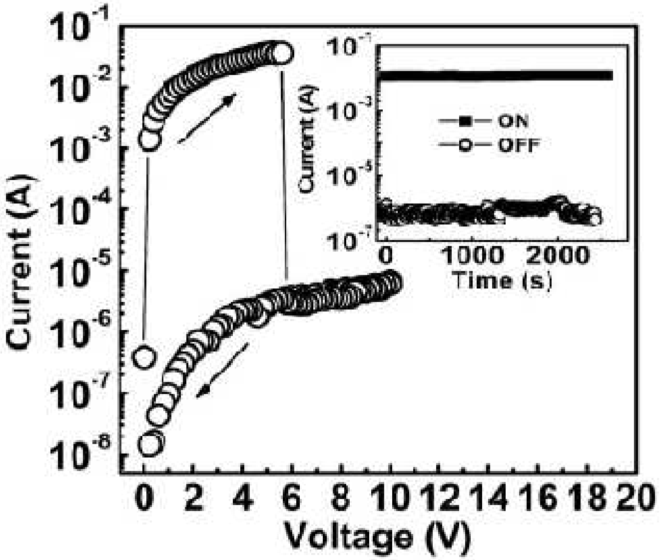
Symmetrical switching

The localized spots may play as filaments that can be conducted by applied voltage higher than V_t(ON)

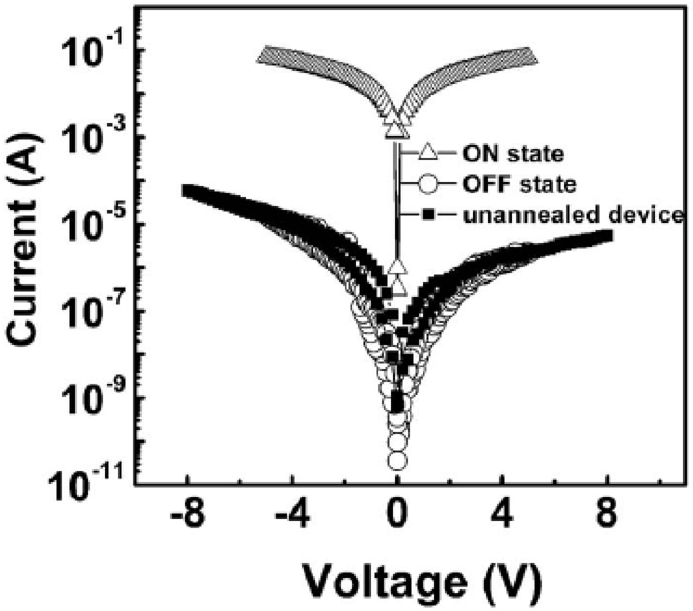
Adv Funct Mater **2007**, *17*, 2637

Resistor-type Memory: Filamentary Conduction Mechanisms

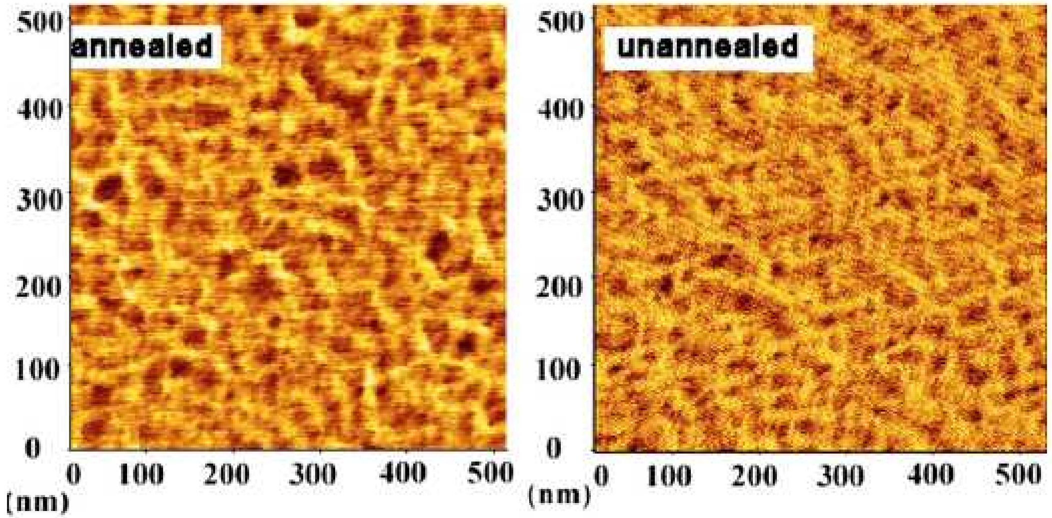
Al/PVK/Al (WORM memory)



The device starts in ON state. As the voltage increases, the current increases linearly with the voltage and decreases abruptly at 5.8 V. (OFF state)



Non-annealed device does show the large current transition.



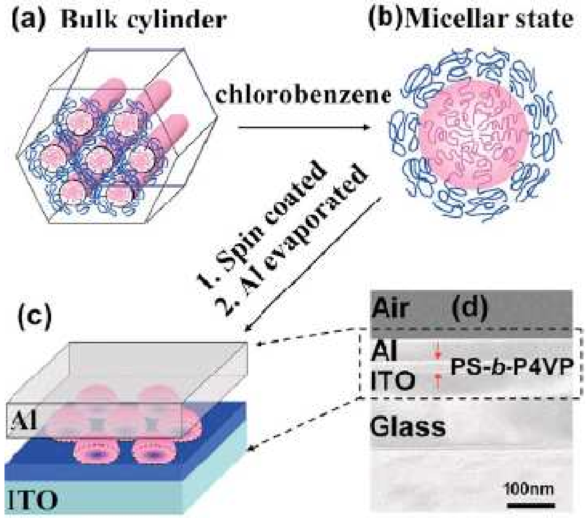
Larger grain size

Metal can migrate inside the polymer layer with sufficient thermal energy and such interdiffusion would increase if the surface of polymer thin film shows a larger grain size

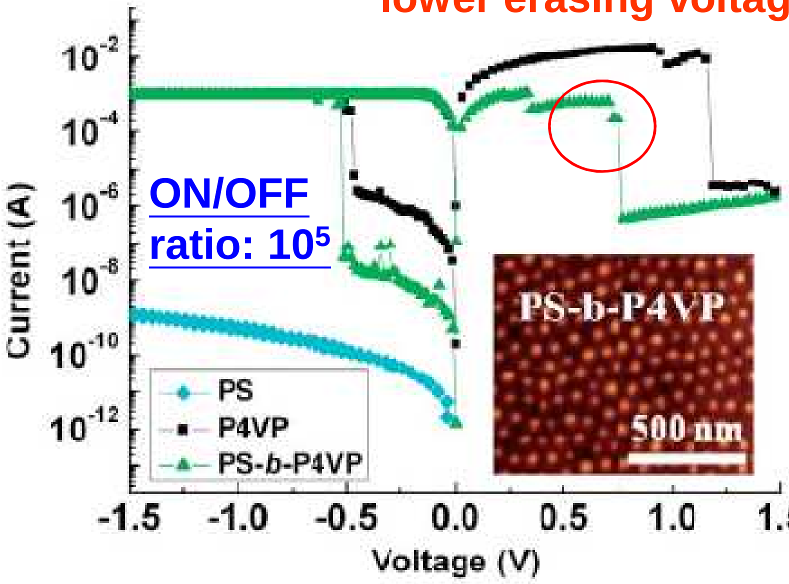
Appl Phys Lett **2008**, *93*, 093505

Resistor-type Memory: Filamentary Conduction Mechanisms

PS(46900)-b-P4VP (20600)

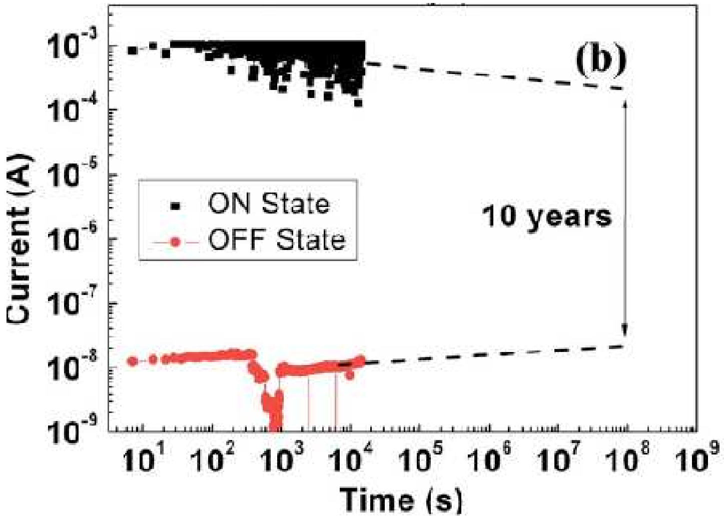


lower erasing voltage



ON/OFF ratio: 10^5

30nm P4VP domain



No significant change after 10^4 sec

PS display a low current indicating a insulator

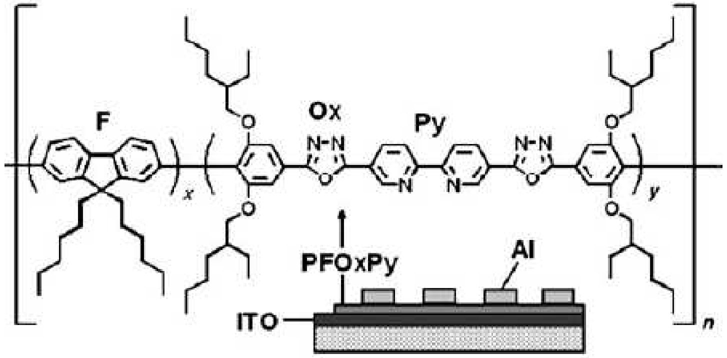
P4VP contains pyridiyl groups, interacts strongly with Al. Al atoms migrate into P4VP zones to form metallic filaments. The nanodomain of P4VP in PS-b-P4VPlimit the growth of Al filament whereas the P4VP homopolymer have no limitation to the extent of growth of Al filament. Filament of lager size would be more difficult to break.

Appl Phys Lett **2008**, *93*, 203303

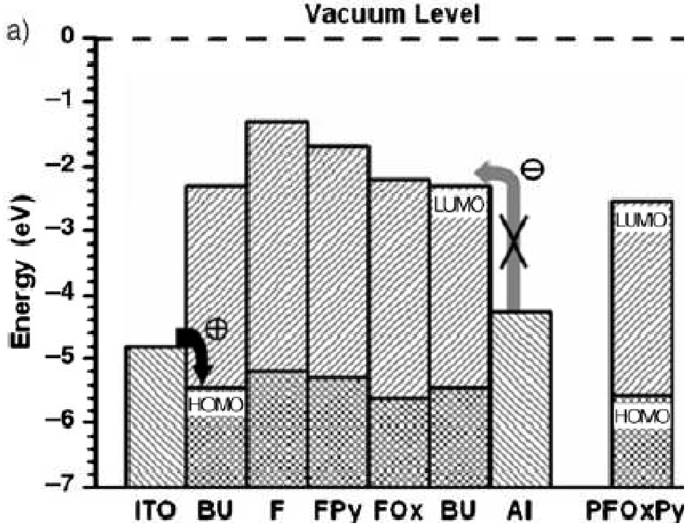
Resistor-type Memory: Space Charges and Traps

Angew Chem Int Ed **2006**, *45*, 2947

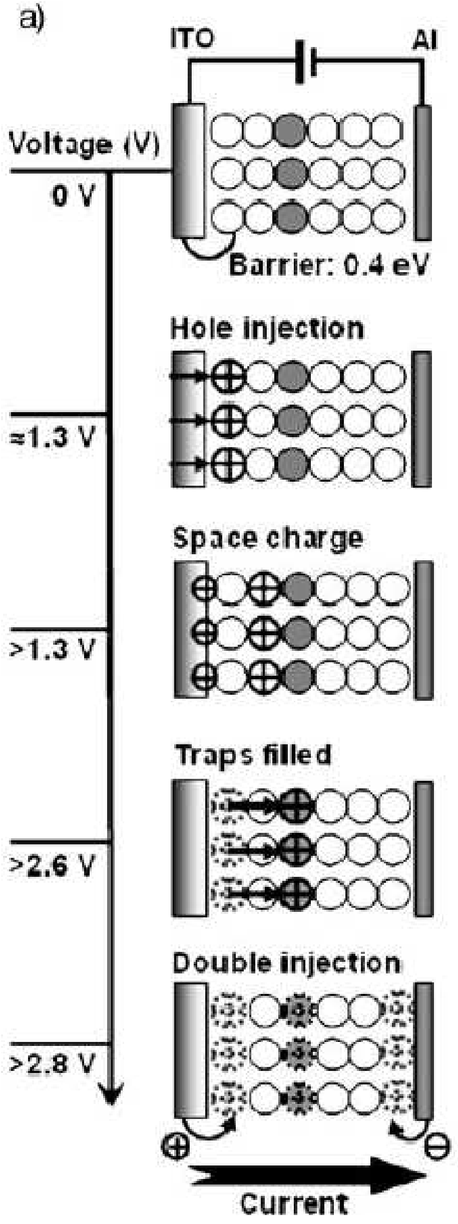
(DRAM) fluorene based D-A conjugated copolymers



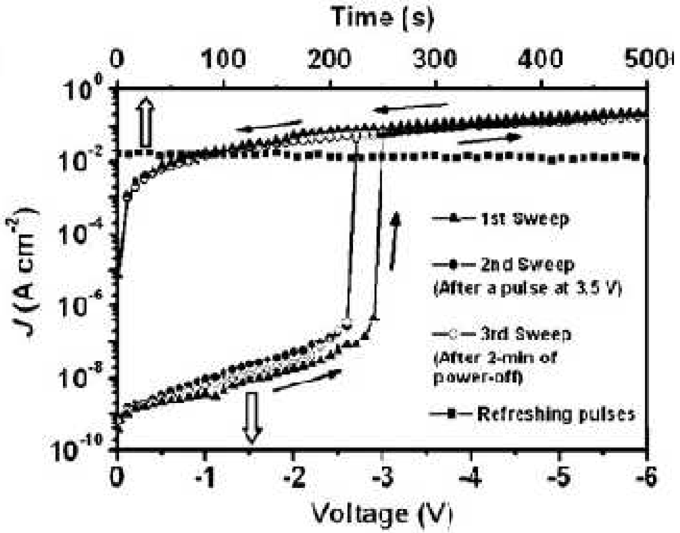
Energy level of LUMO& HOMO and work function of electrode



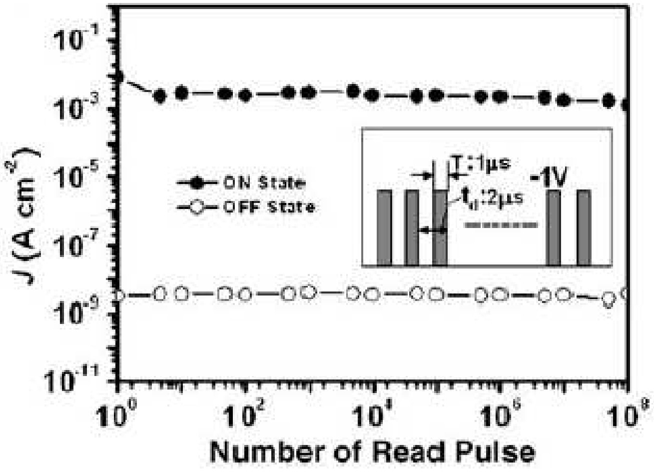
SCLC operation mechanism



I-V Characteristics

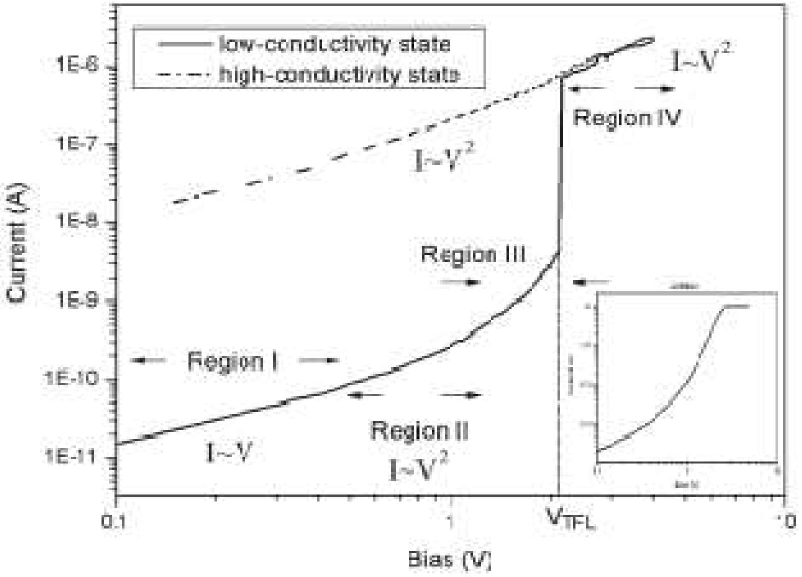


Read cycles on the ON and OFF states



Resistor-type Memory: Space Charges and Traps

Al/PS+Au-NPs/Al (SCLC model)



$$J = \frac{9n\varepsilon\mu}{8n_t}(V^2/L^3) \quad \text{(with traps)}$$

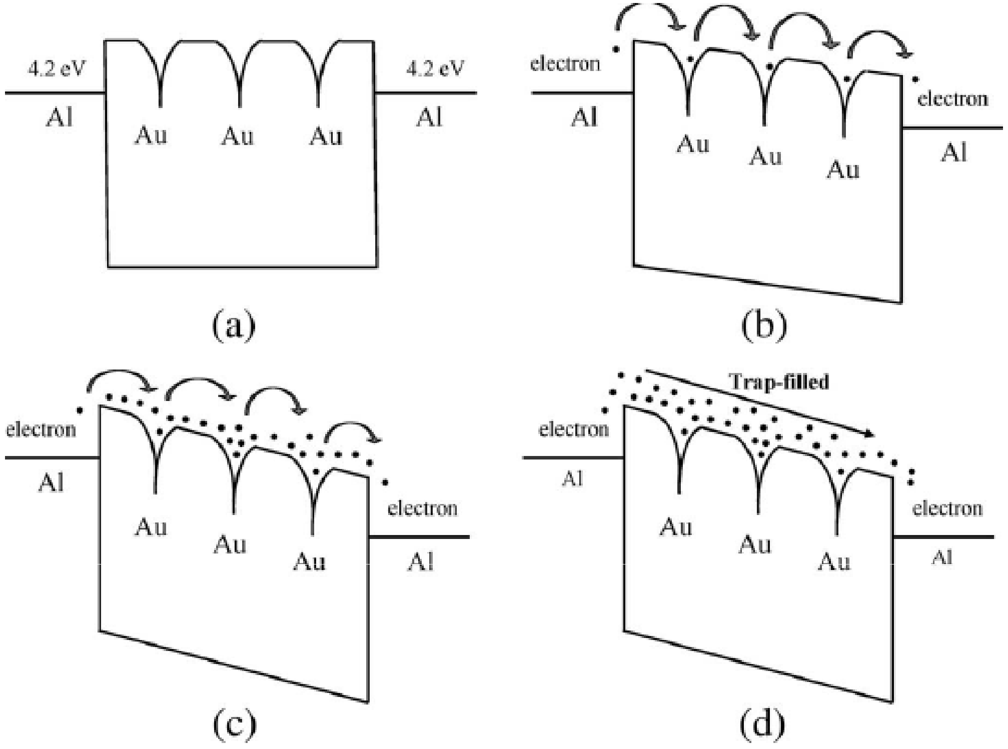
$$J = \frac{9\varepsilon\mu}{8}(V^2/L^3) \quad \text{(traps filled)}$$

J: transport current μ: mobility

n_t: concentration of trapped charges

n: free carriers concentration

V: applied voltage L: dielectric thickness



Region I: current due to the thermally generated free carriers, linear voltage dependent

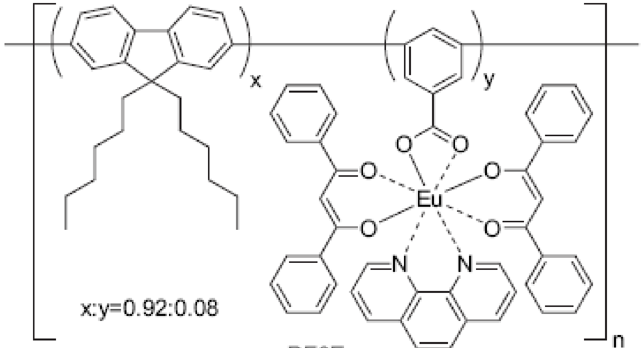
Region II: carriers injected into dielectric from thermionic process; $n \ll n_t$; $I \sim V^2$

Region III: n increase rapidly and traps nearly filled; current exponential dependence on voltage

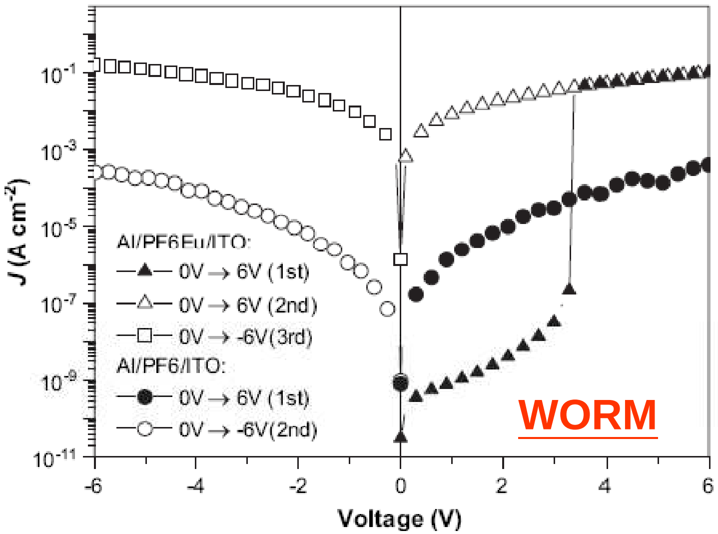
Region IV: trapped filled model

IEEE Electron Device Lett. **2007**, *28*, 569

Resistor-type Memory: Space Charges and Traps



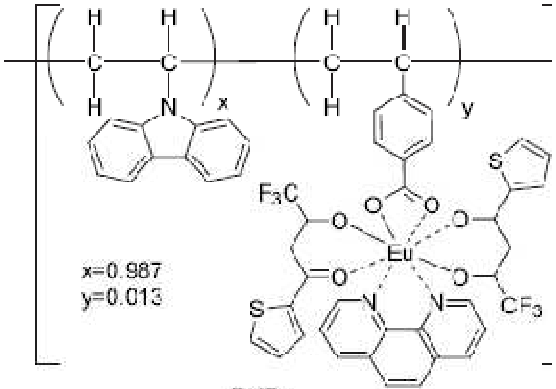
PF6Eu



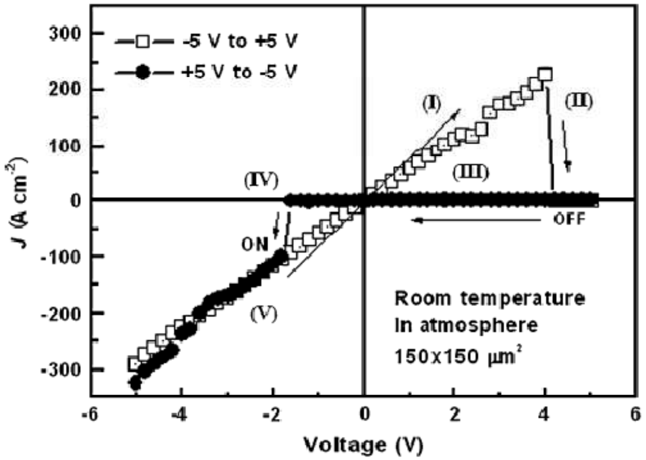
WORM

Polymer **2007**, *48*, 5182; *Adv Mater* **2005**, *17*, 455

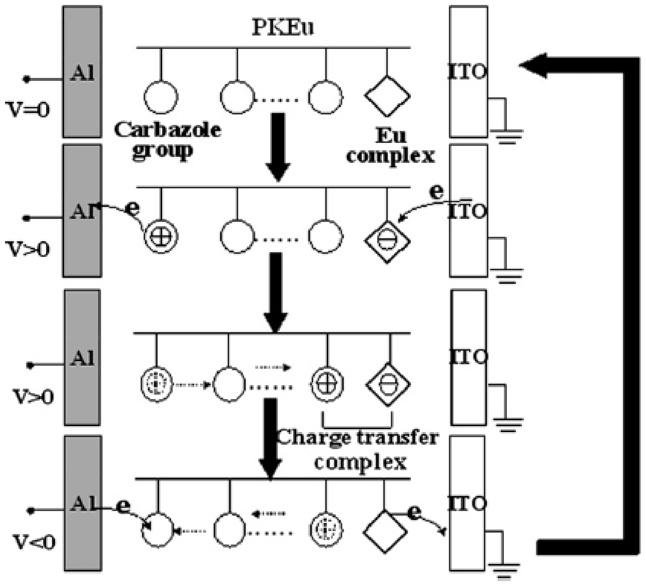
Flash



PKEu



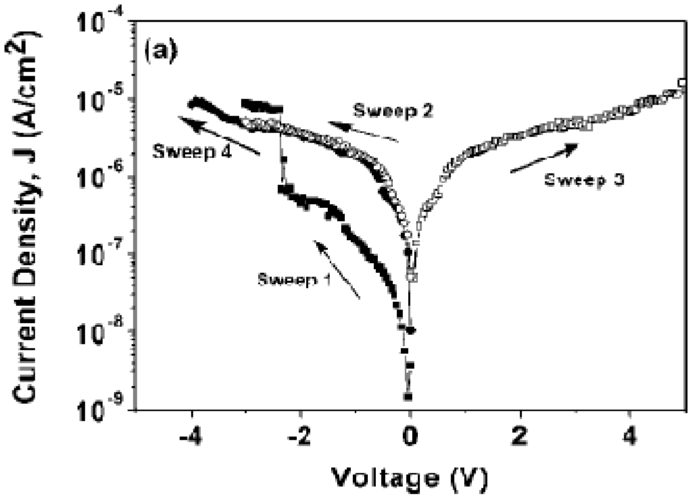
Mechanism

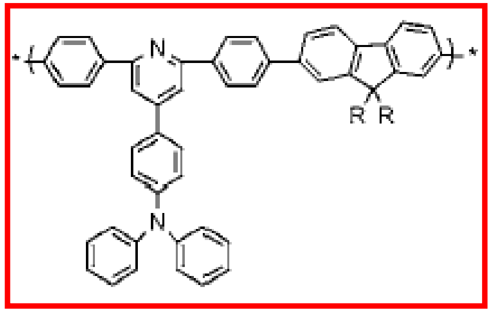


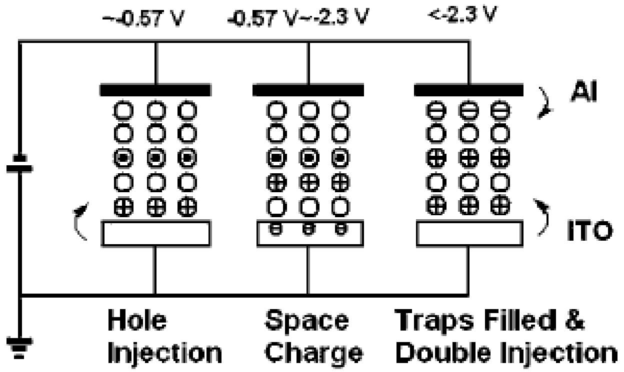
Polymer **2007**, *48*, 5182; *Solid State Lett* **2006**, *9*, 268

Resistor-type Memory: Space Charges and Traps

F12TPN (WORM memory)



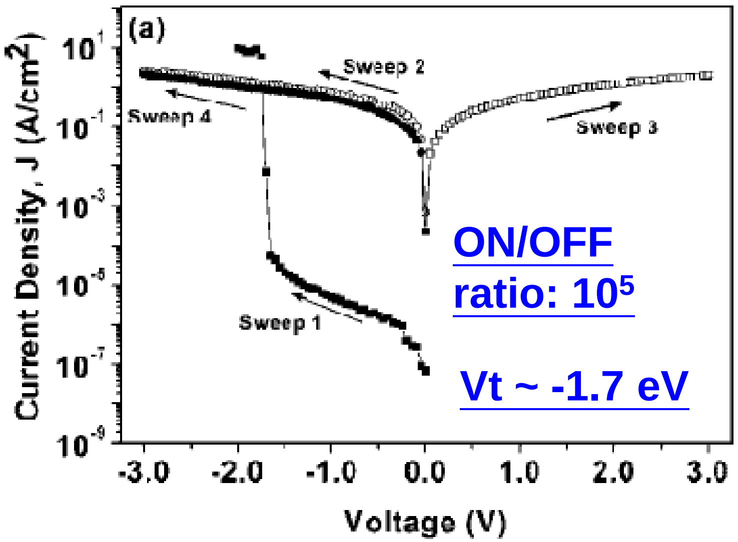




ON/OFF ratio: 10

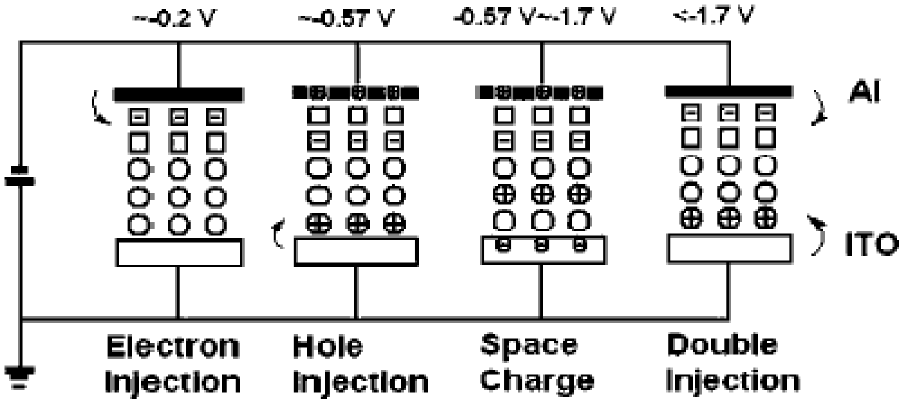
Vt ~ -2.3 eV

F12TPN:CNT Composites



ON/OFF ratio: 10^5

Vt ~ -1.7 eV

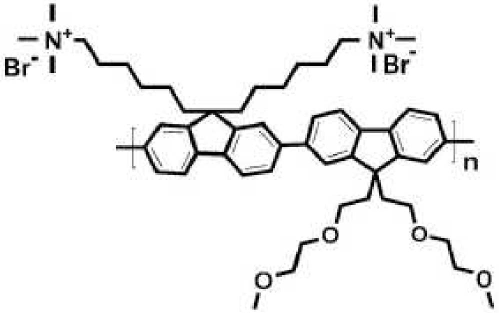


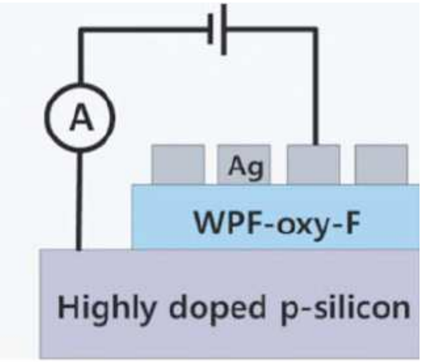
Work function of CNT (5.1 eV)

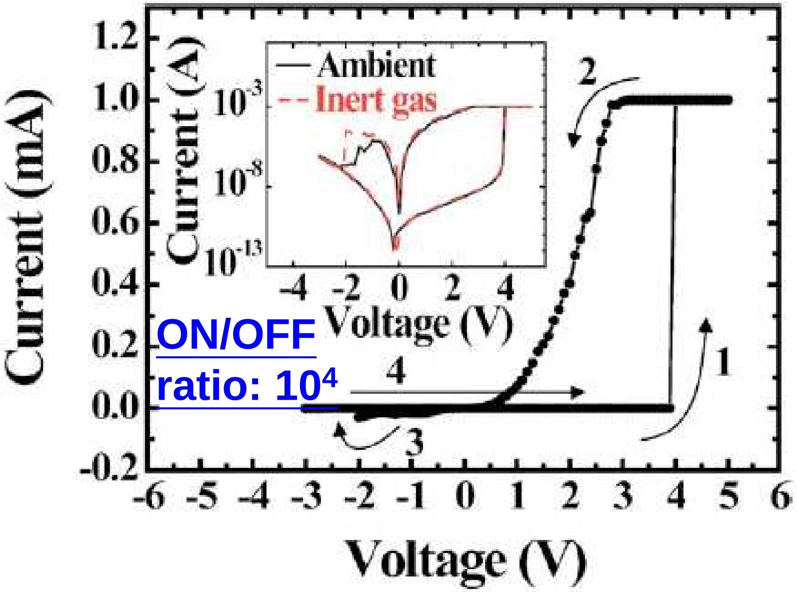
Ohmic contact between Al and CNT interface

J Appl Phys **2007**, *102*, 024502

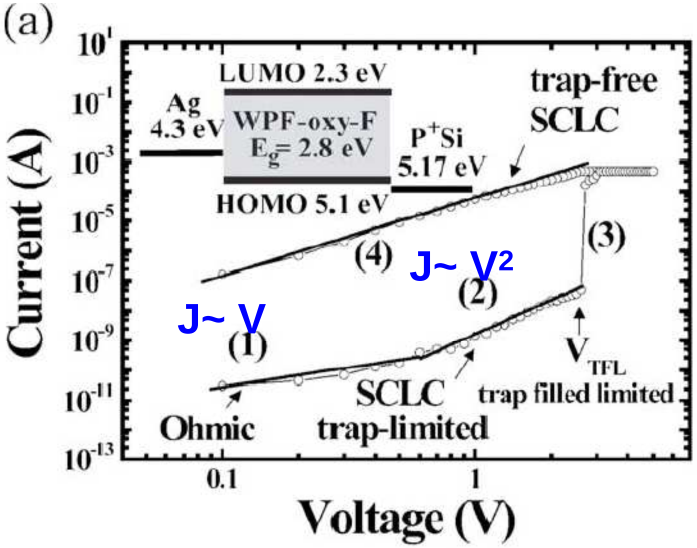
Resistor-type Memory: SCLC and Filament Formation







ON/OFF ratio: 10^4



J~ V

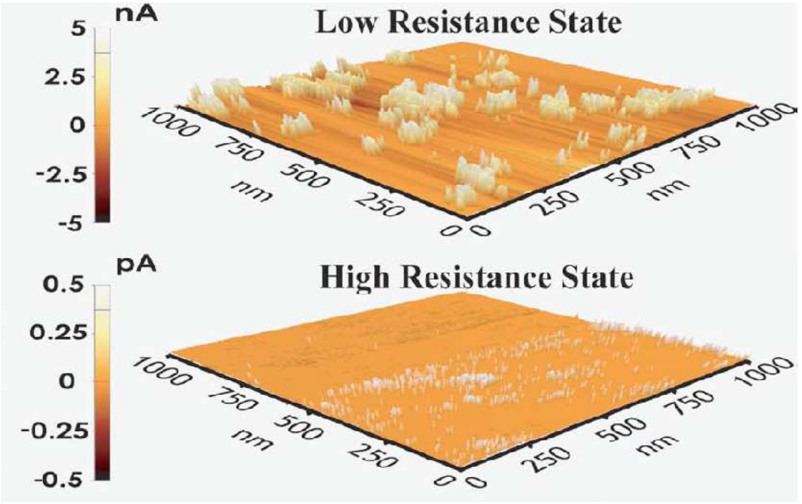
J~ V^2

$$J = \frac{q n_0 \mu V}{d}$$

$$J = \frac{9\varepsilon\varepsilon_0 \mu \Theta V^2}{d^3}$$

Ohmic conduction

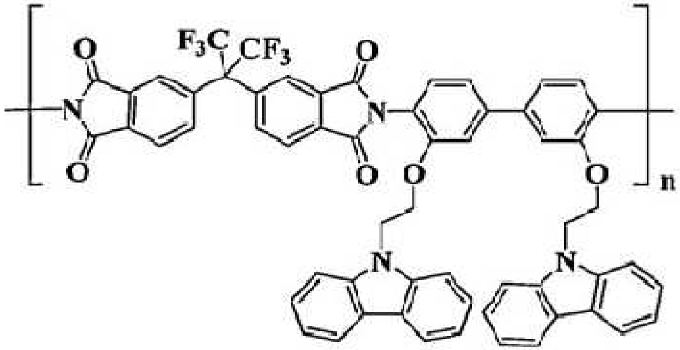
SCLC conduction



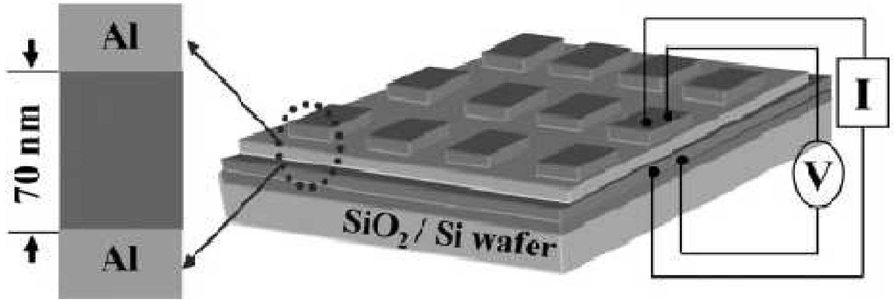
Localized current path

Appl Phys Lett **2008**, *92*, 253308

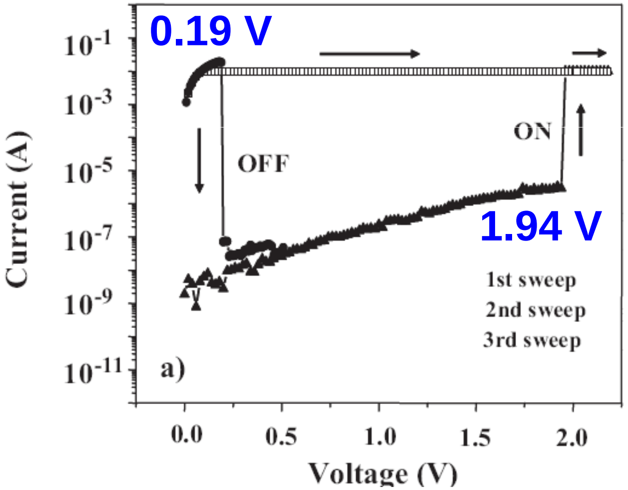
Resistor-type Memory: SCLC and Filament Formation



6F-HAB-CBZ PI

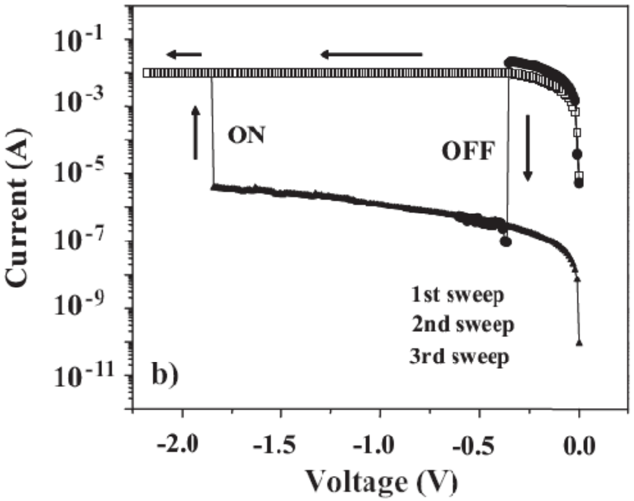


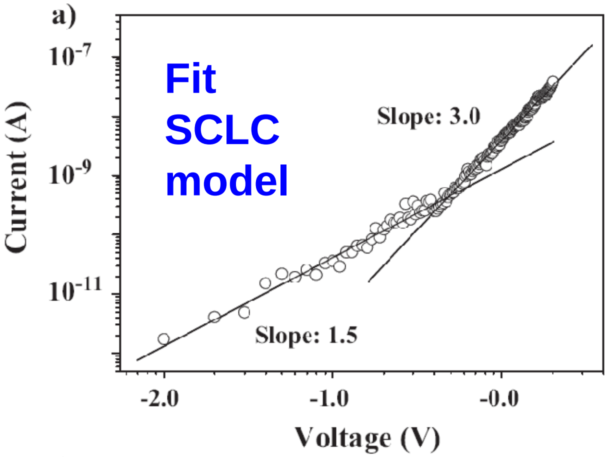
ON/OFF ratio: 10^5-10^{11} depend on current compliance and read voltage



0.19 V

1.94 V





Fit SCLC model

1st: switch-ON, current compliance 0.01A

2nd: confirm ON, current compliance 0.01A

3rd: switch-OFF, current compliance 0.1A

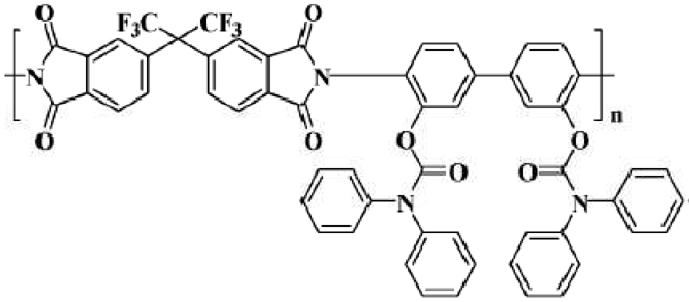
Similar switching behaviors between negative and positive voltage scan

When the applied bias reach Vt, the trapped charges move through the tapped sites by a hopping process (through filament formation), which result in current flow under chosen current compliance

Adv Mater **2008**, *18*, 3276

Resistor-type Memory: SCLC and Filament Formation

Al/6F-HAB-DPC PI/Al (flash memory)



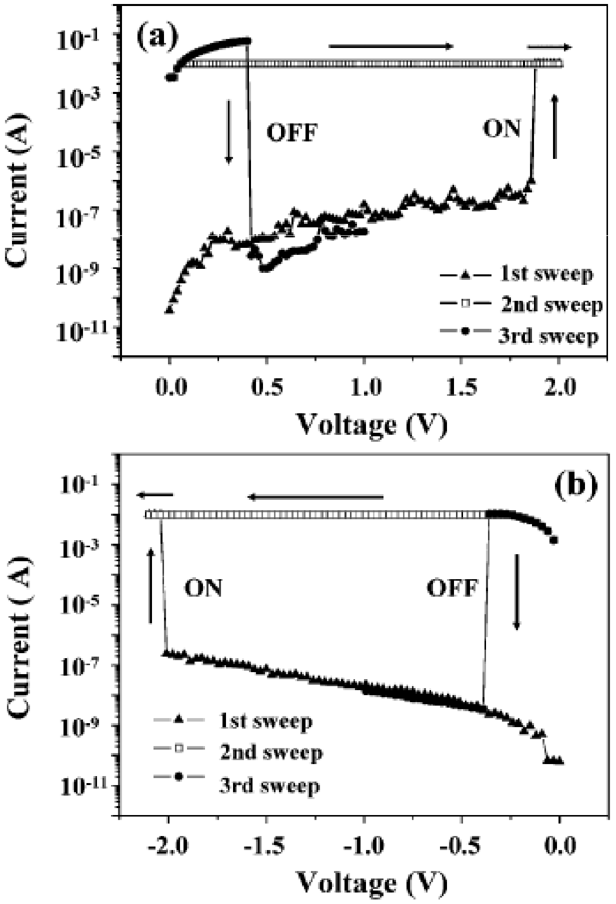
1st: switch-ON, current compliance 0.01A

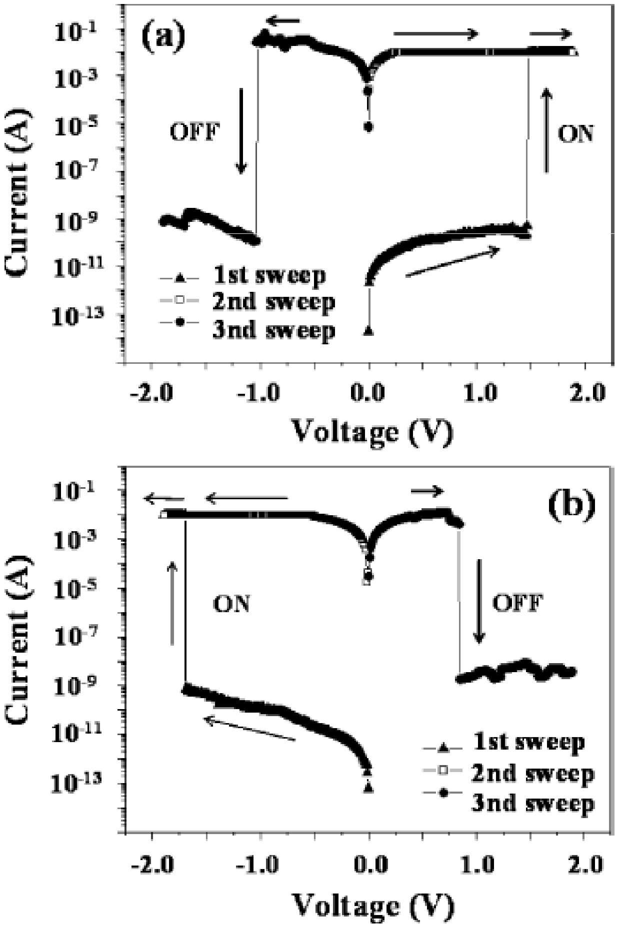
2nd: confirm ON, current compliance 0.01A

3rd: switch-OFF, current compliance 0.1A

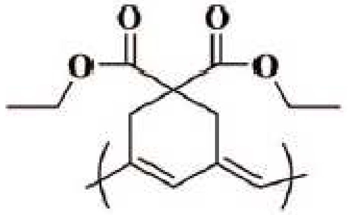
When the turn ON compliance is applied, the trapping of carriers gives rise to the generation of conducting filament. When a higher compliance set, the number of injected charges is too high at biases greater and this overloads the capacity of filament. Such excess current is likely to produce additional heat and result in the repulsive Coulomb interaction which causes rupture of the filament and return to its initial OFF state.

J Mater Chem **2009**, *19*, 2207

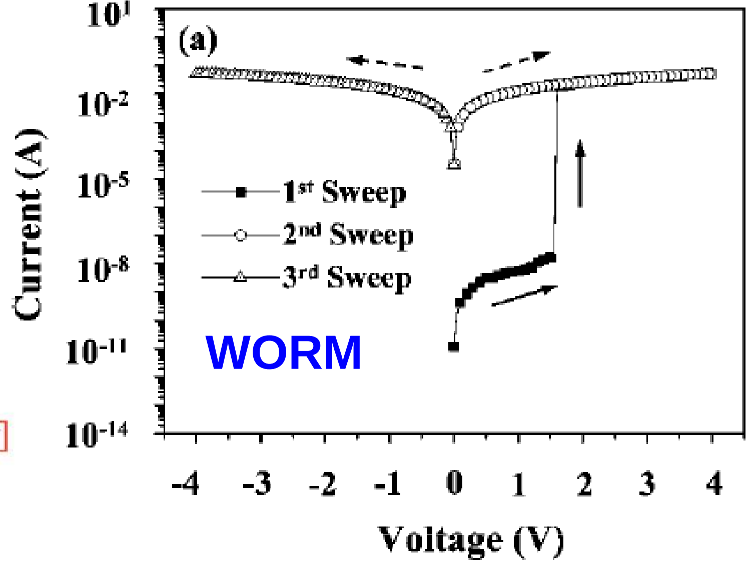




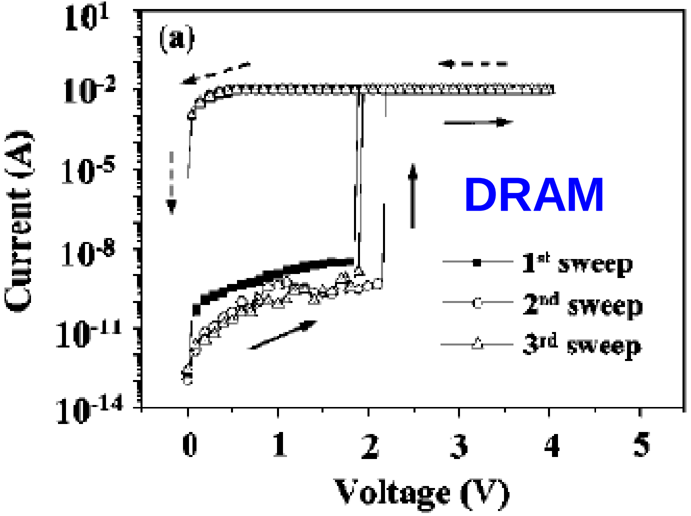
Resistor-type Memory: SCLC and Filament Formation

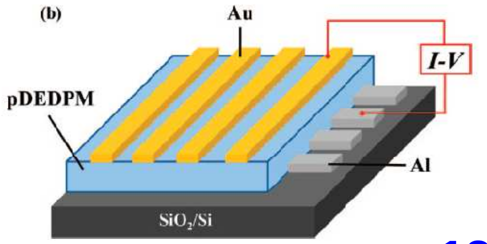


30nm

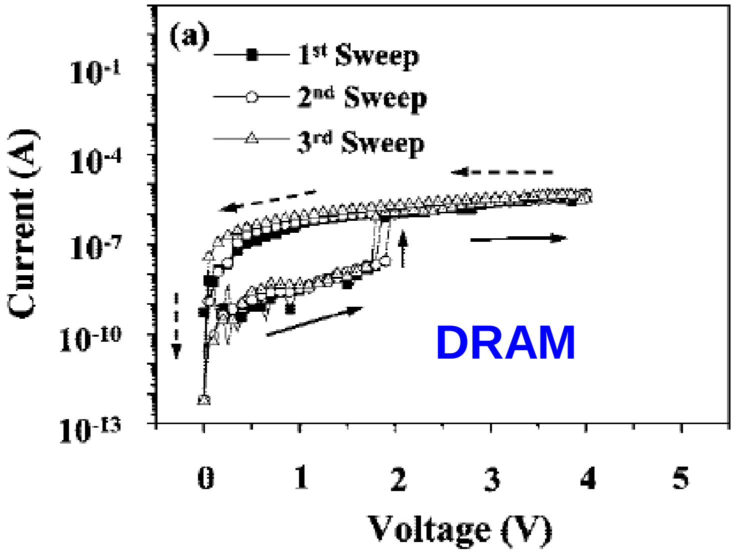


62nm





120nm



The 30 nm of pEDDPM films exhibit WORM with ON/OFF ratio of 10^6

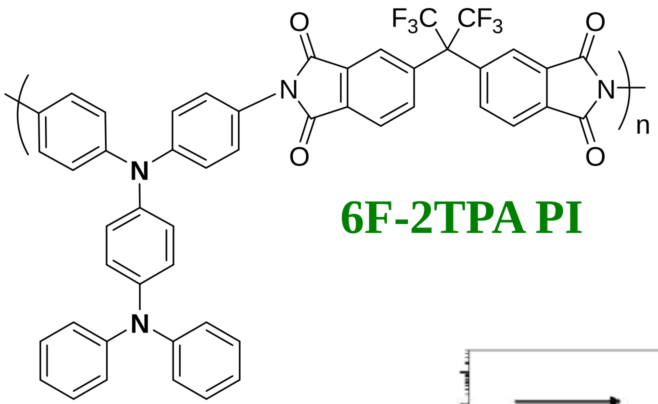
The 62 nm of pEDDPM films exhibit DRAM with ON/OFF ratio of 10^8

The 120 nm of pEDDPM films exhibit DRAM but ON/OFF ratio is as low as 100

J Phys Chem C **2009**, *113*, 3855

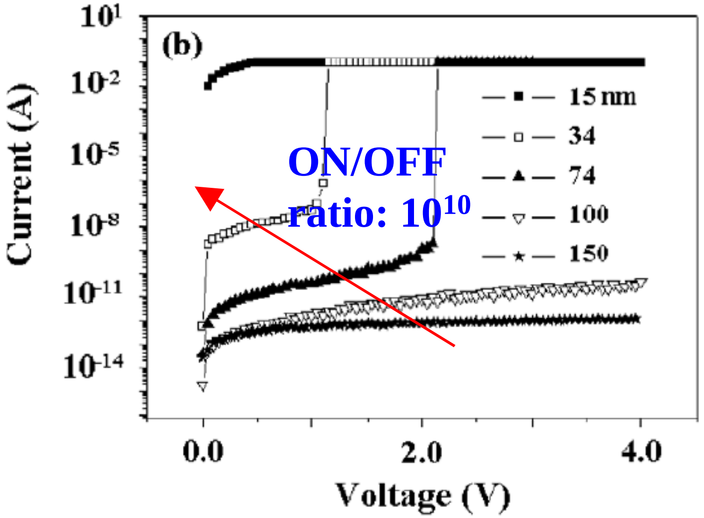
Resistor-type Memory: SCLC and Filament Formation

Previous Works

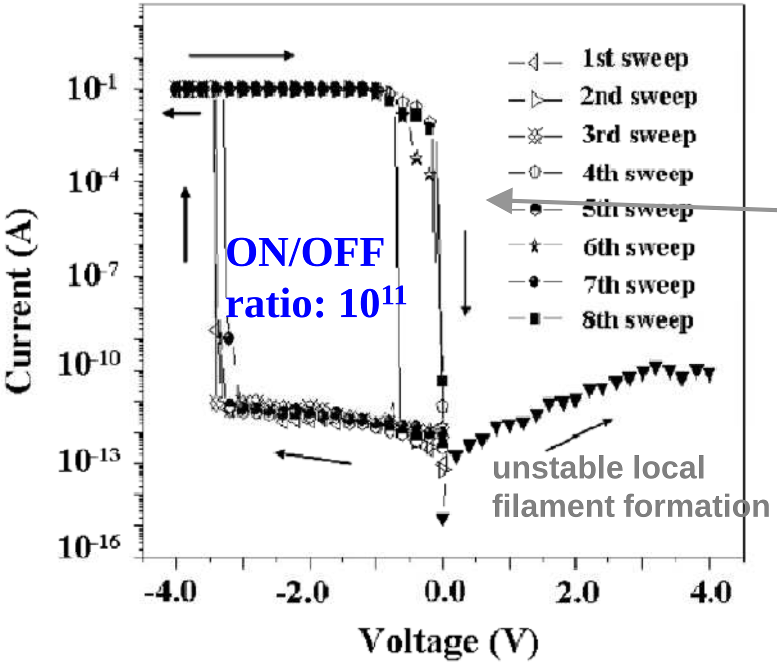


6F-2TPA PI

WORM and DRAM memory characteristics as well as polarity-dependent turn on behavior when thickness of the polymer layer in the devices are varied.



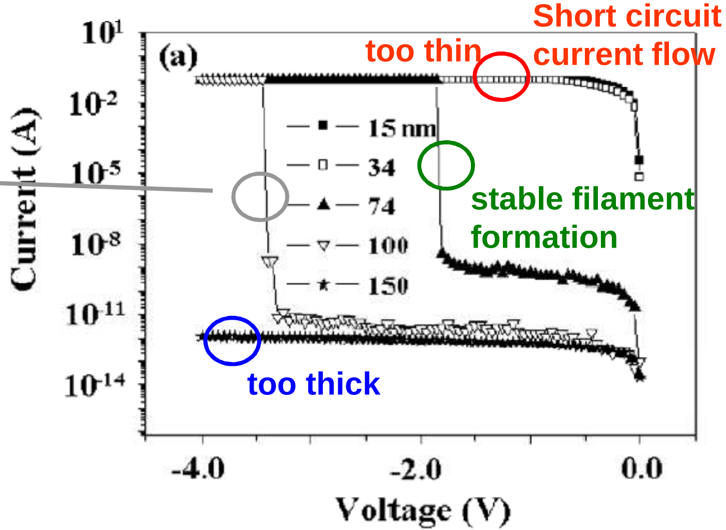
ON/OFF ratio: 10^{10}



ON/OFF ratio: 10^{11}

unstable local filament formation

100 nm thick shows DRAM characteristics



too thin

Short circuit current flow

stable filament formation

too thick

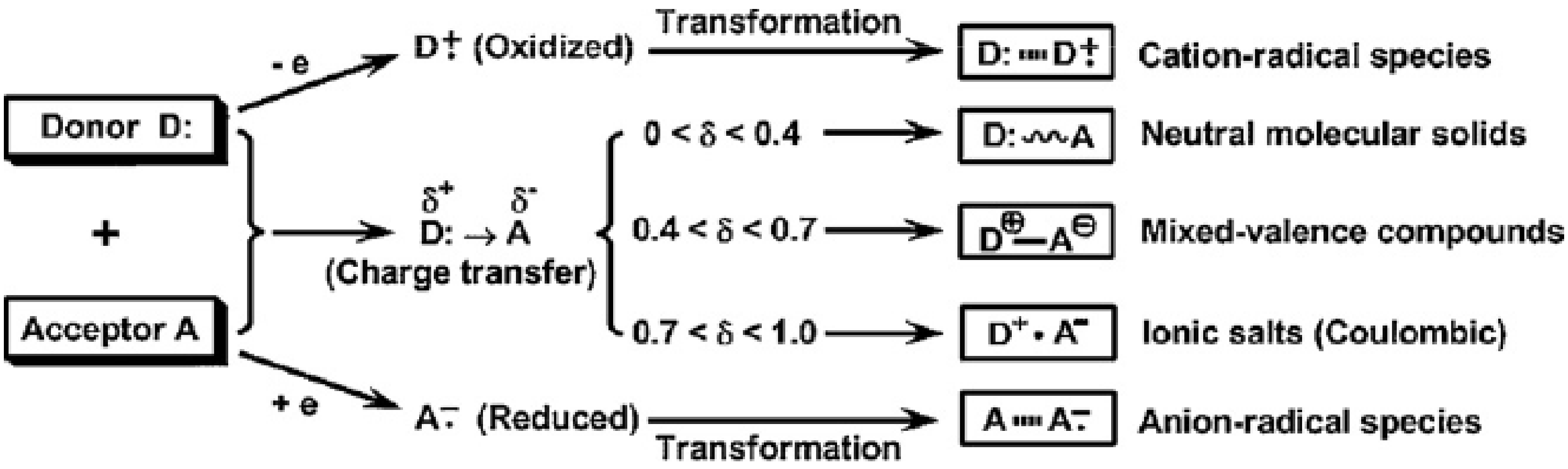
Thinner film shows lower switching threshold voltages (WROM)

Nanotechnology **2009**, *20*, 135204

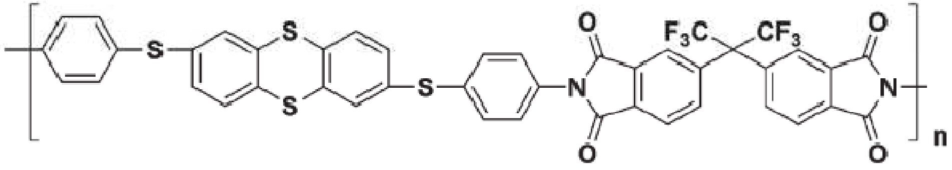
Resistor-type Memory: Charge Transfer Effect

A charge transfer effect is defined as an electron donor (D)-electron acceptor complex, characterized by electronic transition to a excited states in which there is a partial transfer of electronic charge from the donor to acceptor moiety.

Fomation of ion-radical species and charge transfer complex



Resistor-type Memory: Charge Transfer Effect

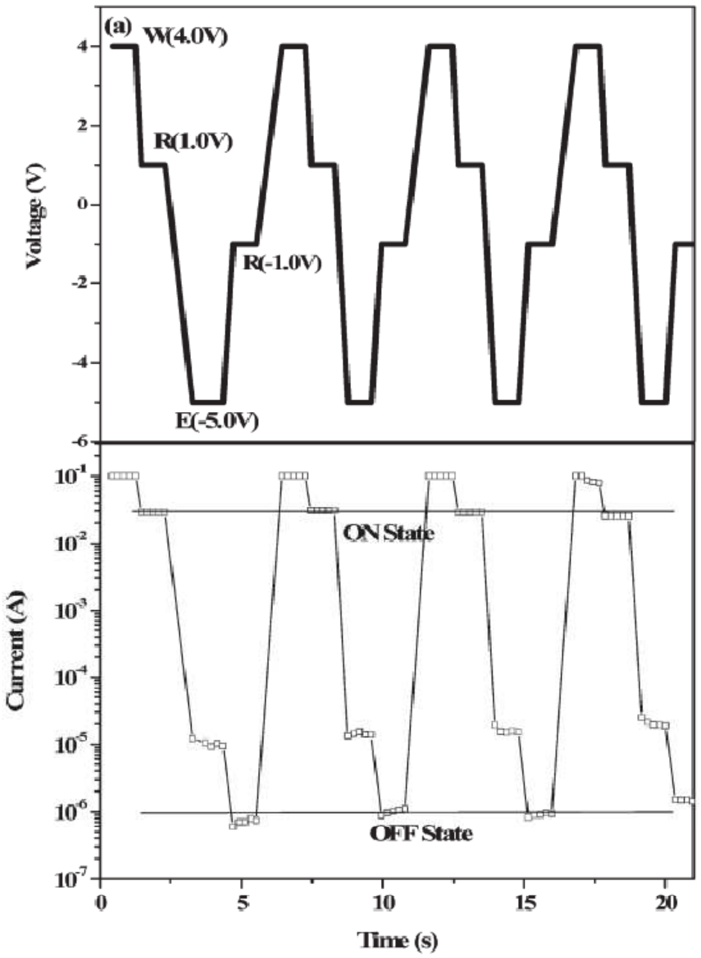


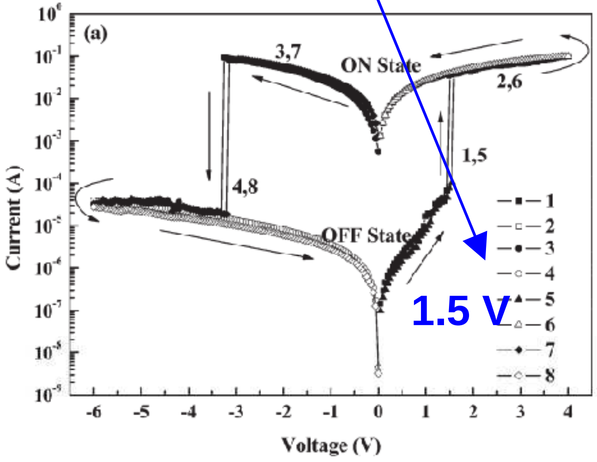
Dipole moment: 5.83 Debye

(-5.55, -2.04) eV

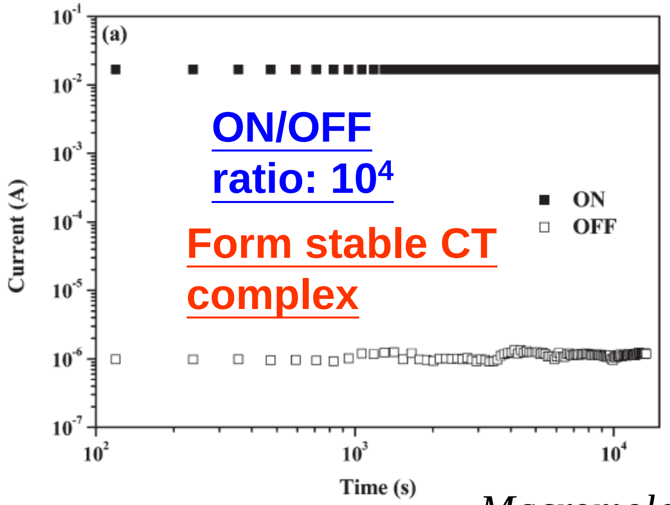
ITO/APTT-6FDA/Al (flash memory)

WRER cycles



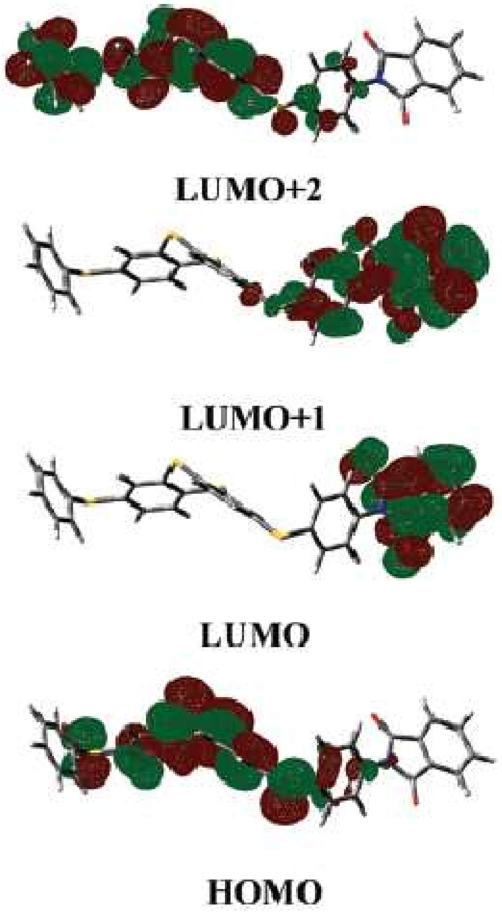


1.5 V



ON/OFF ratio: 10^4

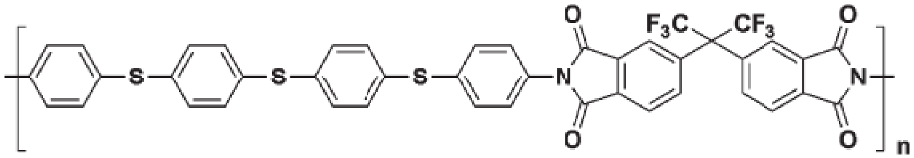
Form stable CT complex



Polarized charge transfer

Macromolecules **2009**, *ASAP Article*

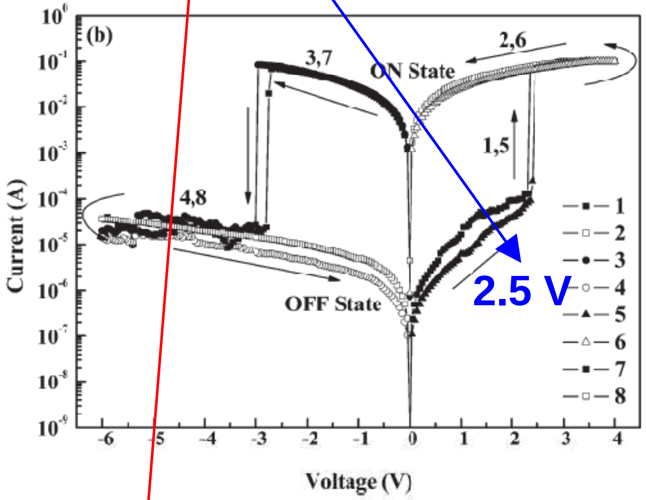
Resistor-type Memory: Charge Transfer Effect



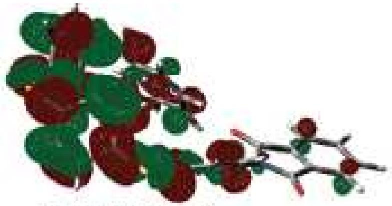
ITO/3SDA-6FDA/Al (flash memory)

Dipole moment: 6.00 Debye

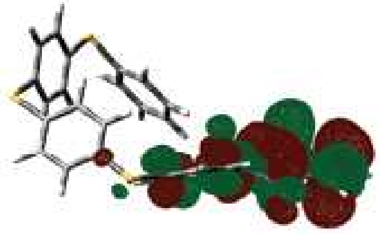
(-5.71, -2.25) eV



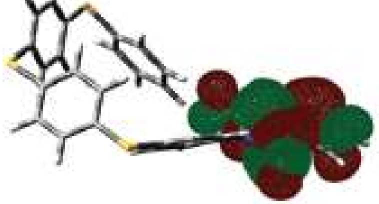
2.5 V



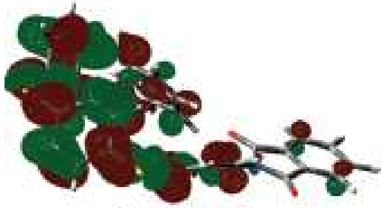
LUMO+2



LUMO+1

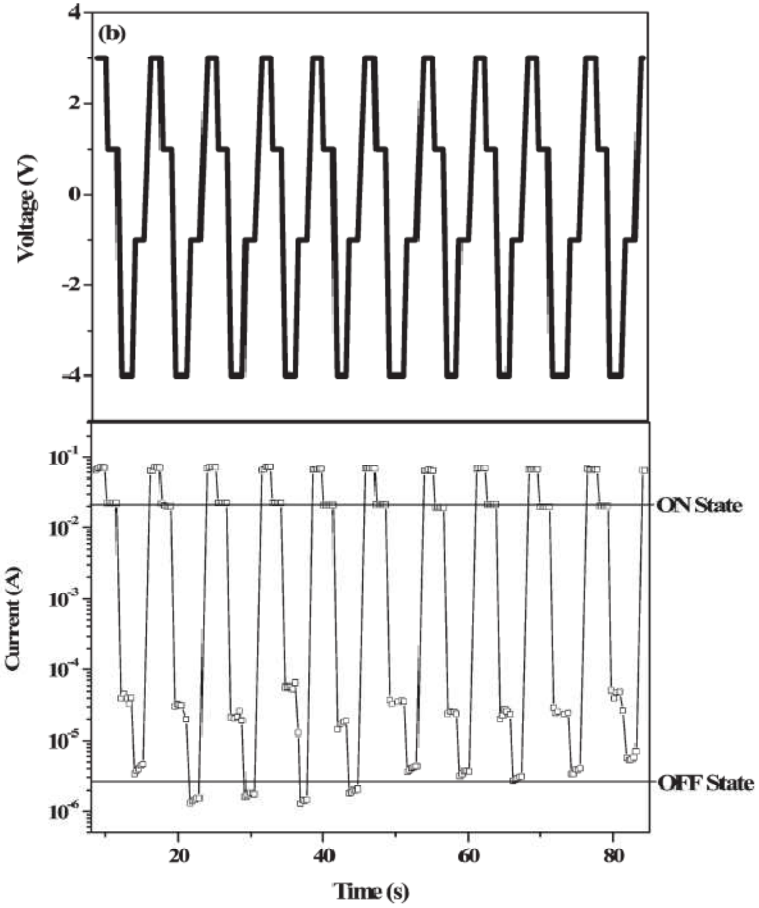


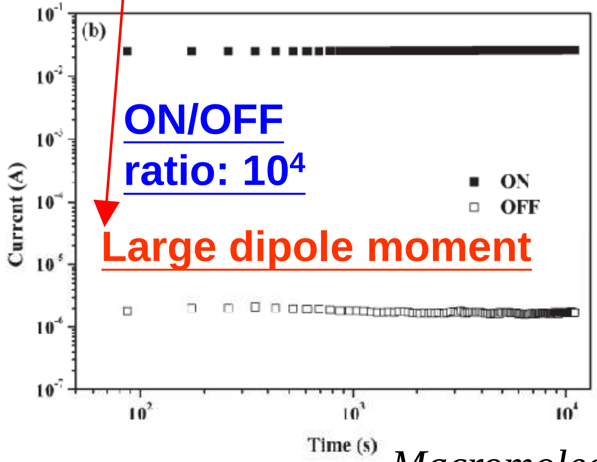
LUMO



HOMO

WRER cycles





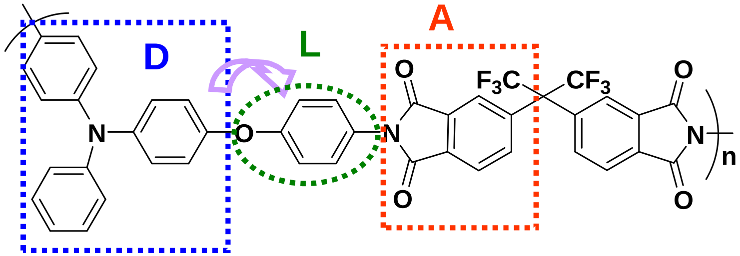
ON/OFF ratio: 10^4

Large dipole moment

Macromolecules **2009**, *ASAP Article*

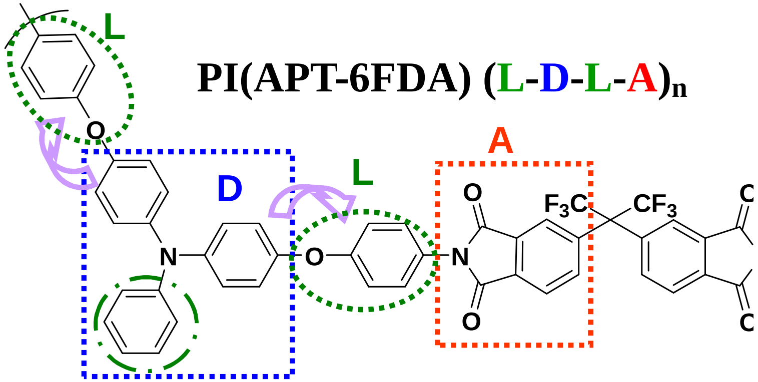
W. C. Chen, Macromolecules **2010**, *43*, 1236

PI(AAPT-6FDA) (D-L-A)$_n$



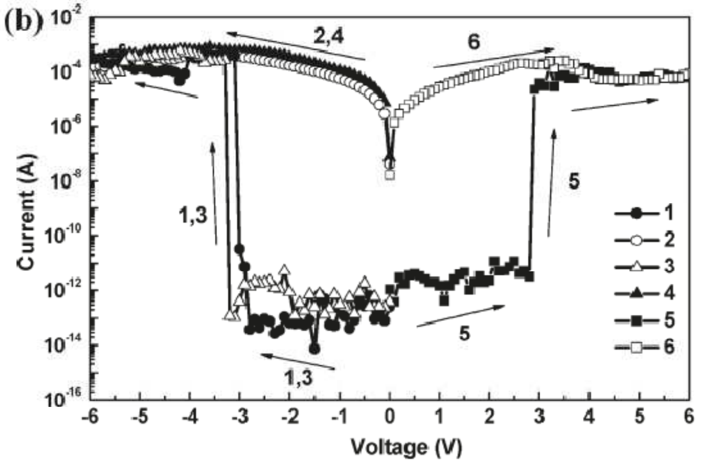
2.65 Deybe (-4.92, -2.26)

PI(APT-6FDA) (L-D-L-A)$_n$



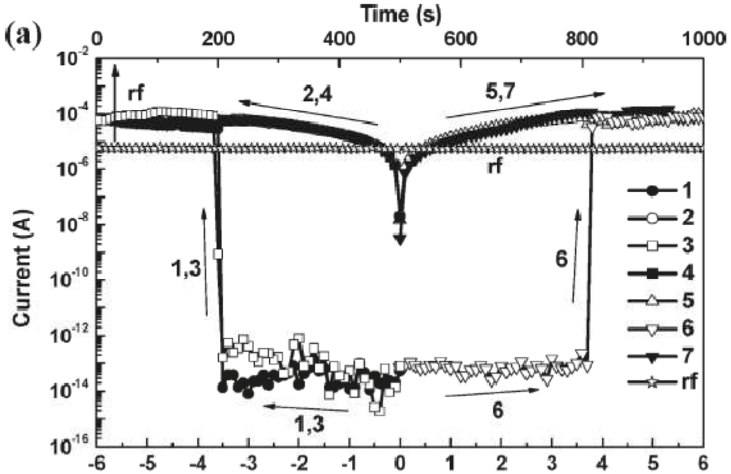
2.87 Deybe (-4.87, -2.26)

- **Weak dipole moment provides an unstable CT complex for the volatile memory device.**
- **The dual-mediated phenoxy linkages of PI(APT-6FDA) produced a potential barrier for delaying the back charge transfer (CT) process by the electric field.**



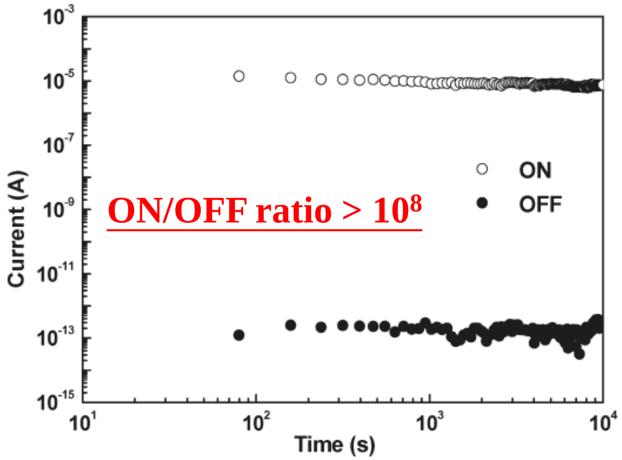
I-V curves of PI(AAPT-6FDA) (DRAM)

3&5 : less than 30s after turning off the power



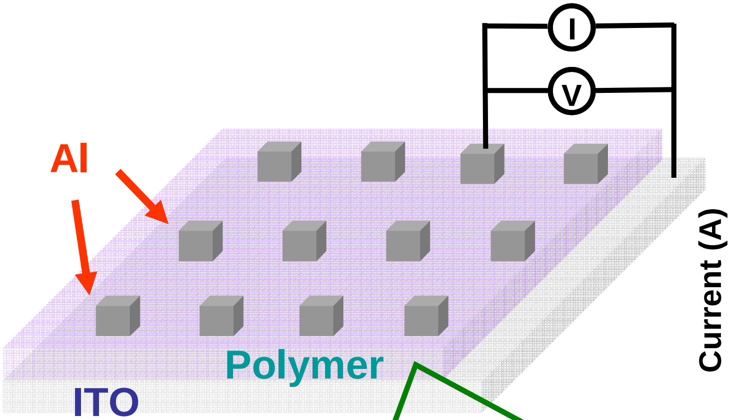
I-V curves of PI(APT-6FDA) (SRAM)

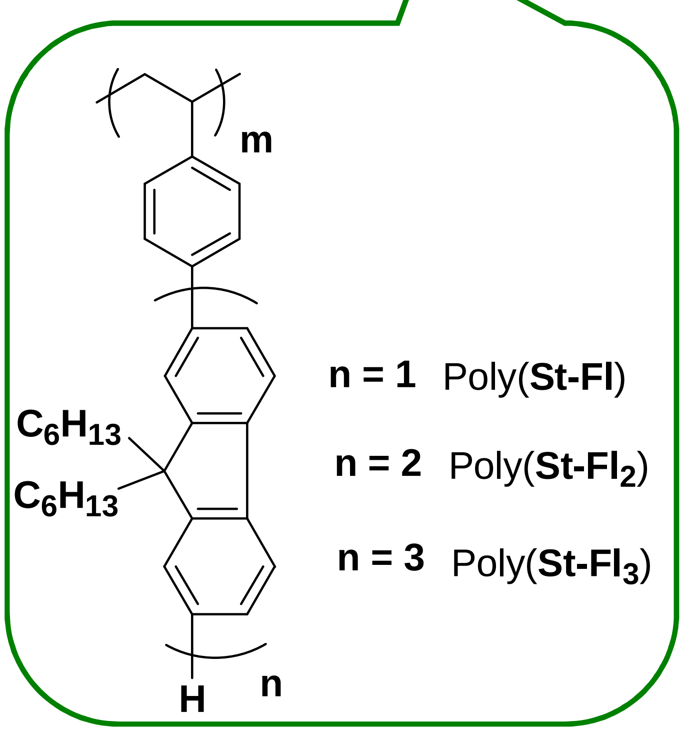
3&6 : 4min after turning off the power



ON/OFF ratio > 10^8

Resistor-type Memory: Charge Transfer Effect

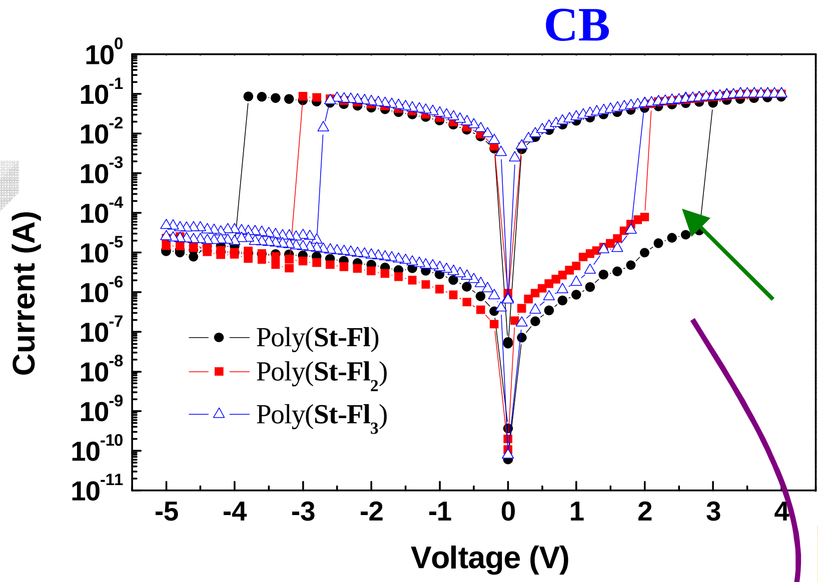


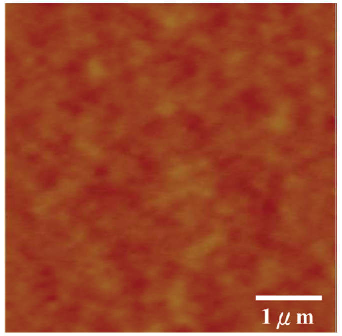


n = 1 Poly(**St-Fl**)

n = 2 Poly(**St-Fl$_2$**)

n = 3 Poly(**St-Fl$_3$**)

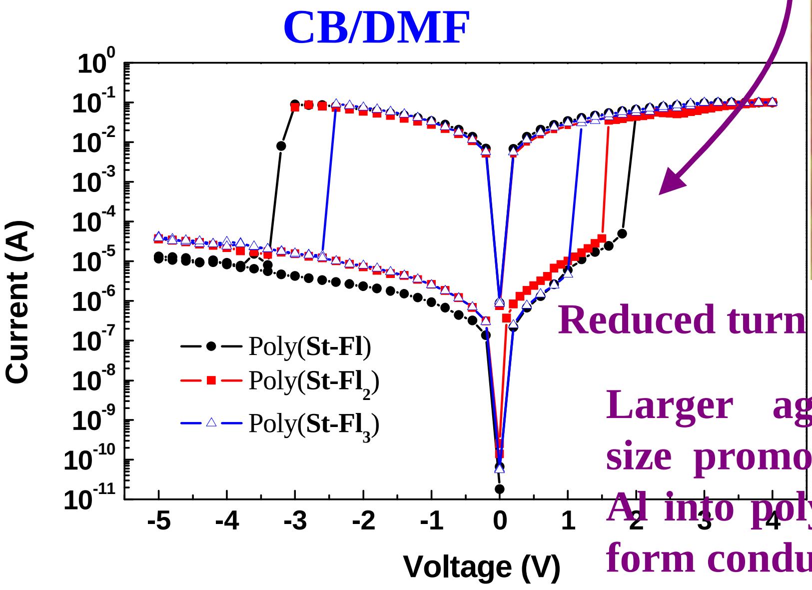


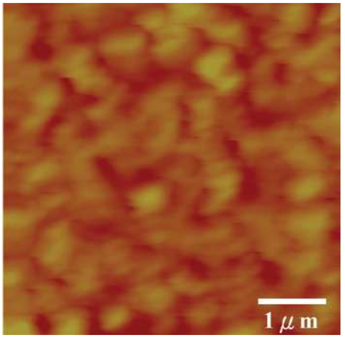


P(St-Fl) -5.86 eV

P(St-Fl)$_2$ -5.80 eV

P(St-Fl)$_3$ -5.77 eV





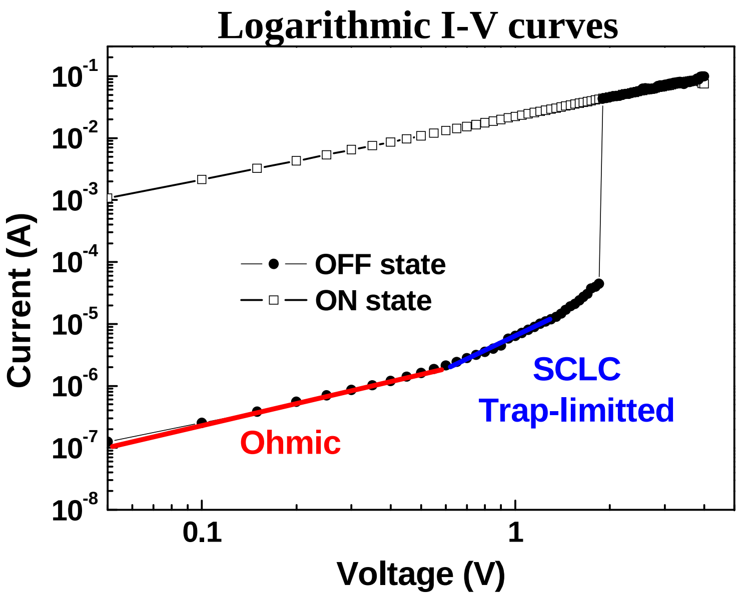
Reduced turn on voltage

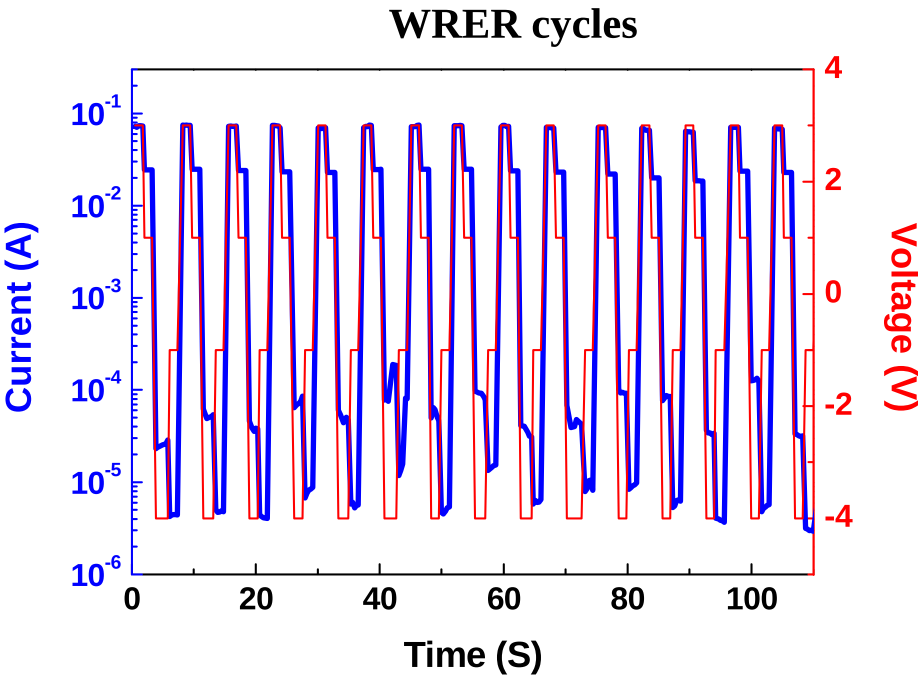
Larger aggregation domain size promote diffusion of the Al into polymer thin film and form conduction channel

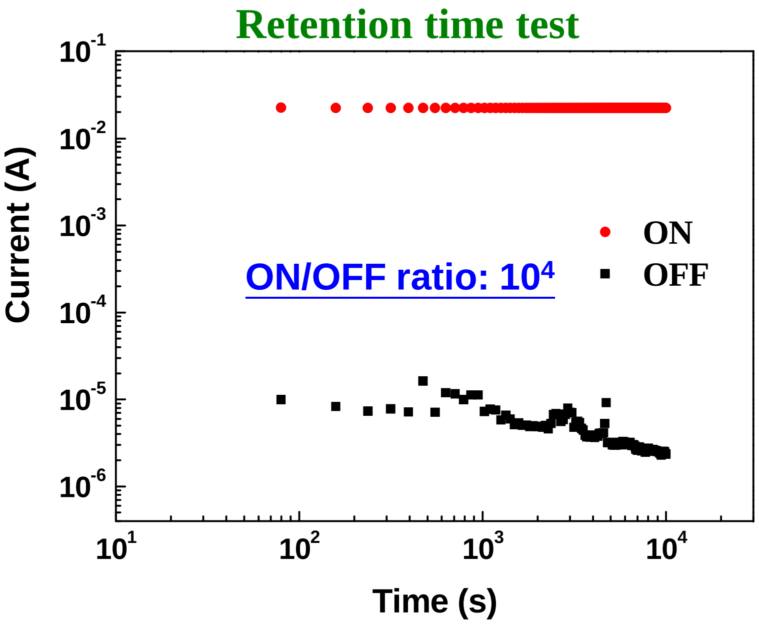
Cooperated with Professor Akira Hirao (Tokyo Tech)

ACS Appl Mater &Interfaces **2009**, *1*, 1974

Resistor-type Memory: Charge Transfer Effect


Logarithmic I-V curves

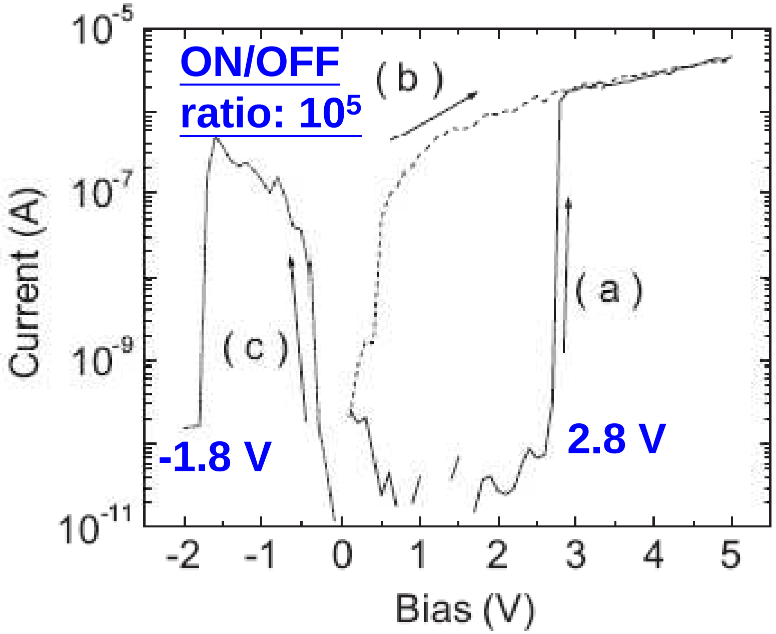

WRER cycles

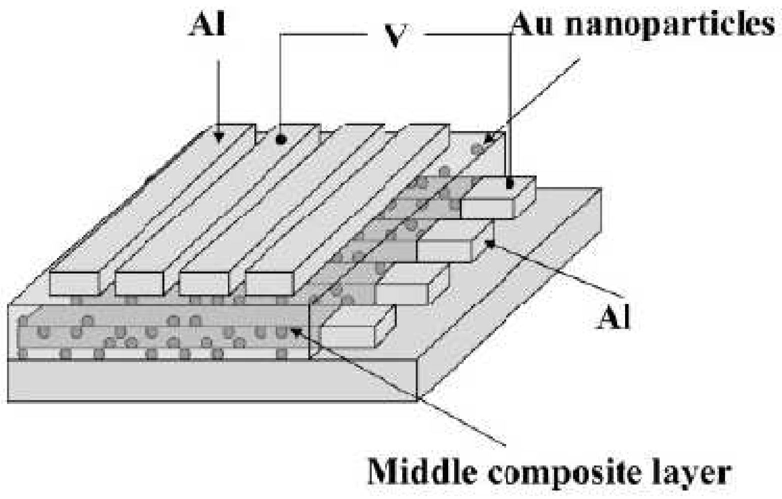

Retention time test

- Non-volatile flash type memory device
- space charge limit current (SCLC) theory with metallic filament mechanism
- Good stability for at least 10^4 S
- Establish chemical structure-memory effect relationship

Resistor-type Memory: Charge Transfer Effect

Al/Au-DT+8HQ+PS/Al (flash memory)

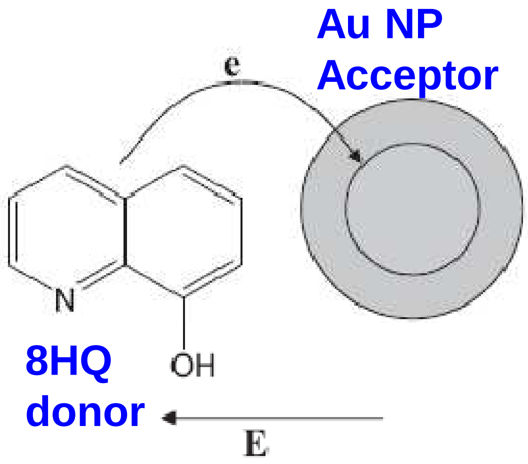


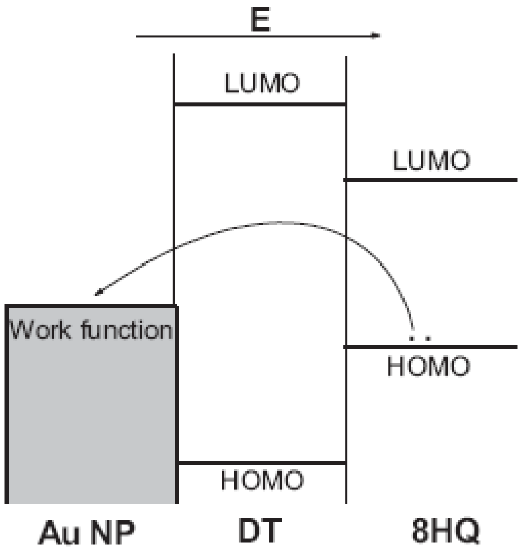


PS acts as an inert matrix

ON state: Charge transfer between Au-NP and 8HQ under high electric field

OFF state: A reverse field cause tunneling of electron from gold NP back to HOMO of 8HQ+

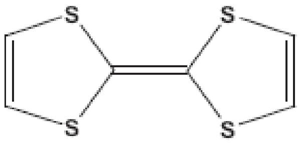




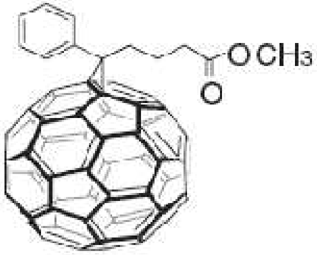
Adv Mater **2006**, *16*, 1001; *Nat Mater* **2004**, *3*, 918

Resistor-type Memory: Charge Transfer Effect

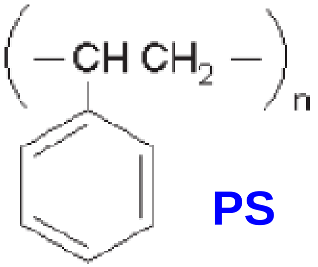
Al/PS+TTF+PCBM/Al (flash memory)



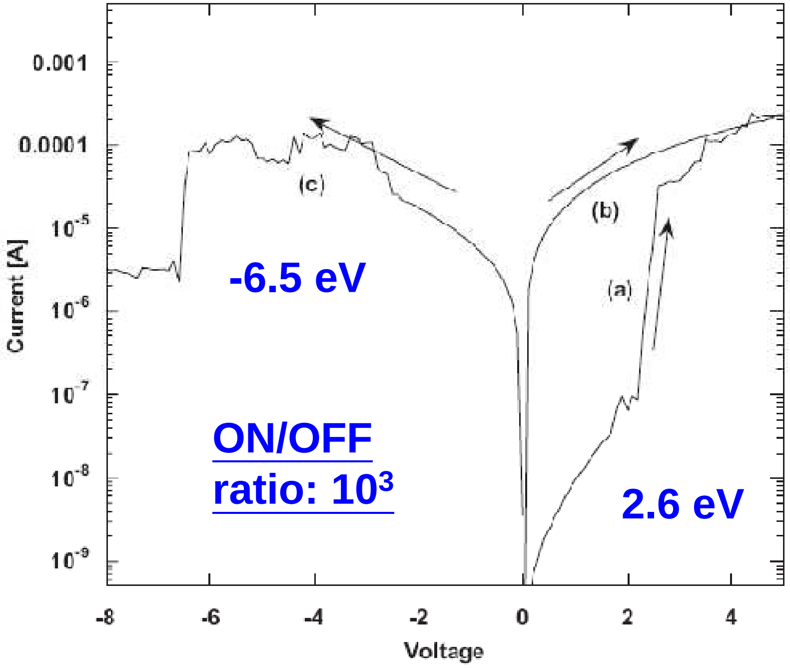
TTF



PCBM



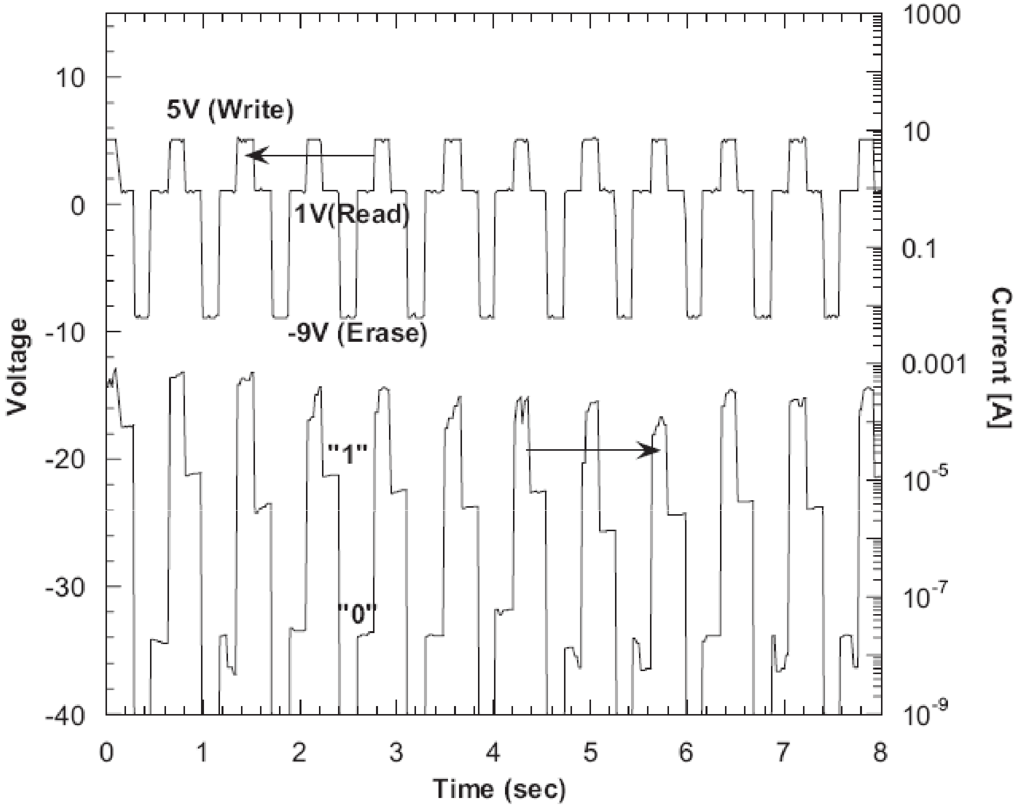
PS



-6.5 eV

ON/OFF ratio: 10^3

2.6 eV



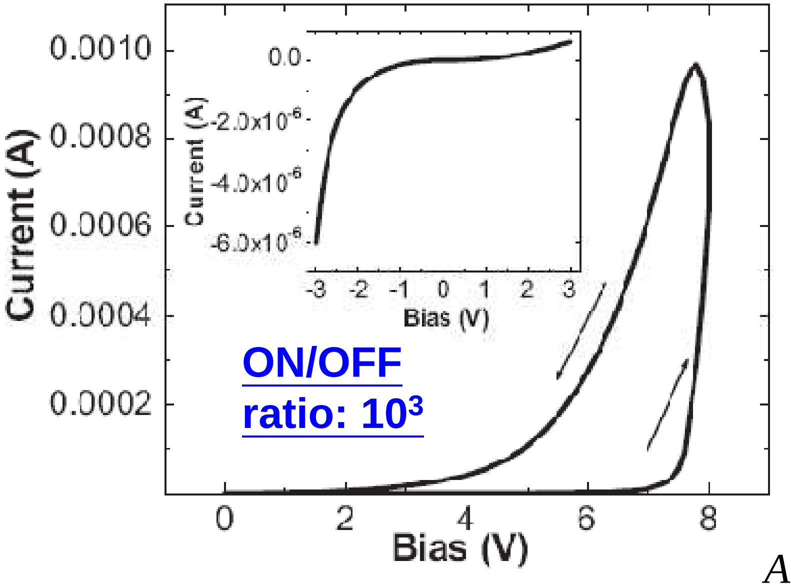
TTF (-5.09, -2.33) eV ; PCBM (-6.1, -3.7) eV

Charge transfer between TTF and PCBM

Adv Mater **2005**, *17*, 1440

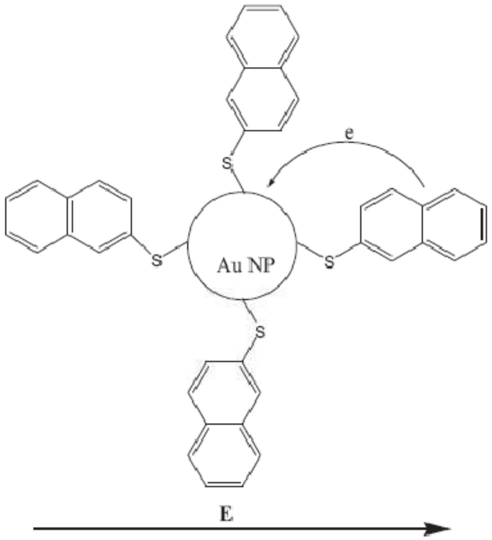
Resistor-type Memory: Charge Transfer Effect

Al/Au-2NT NP+PS/Al (WORM memory)



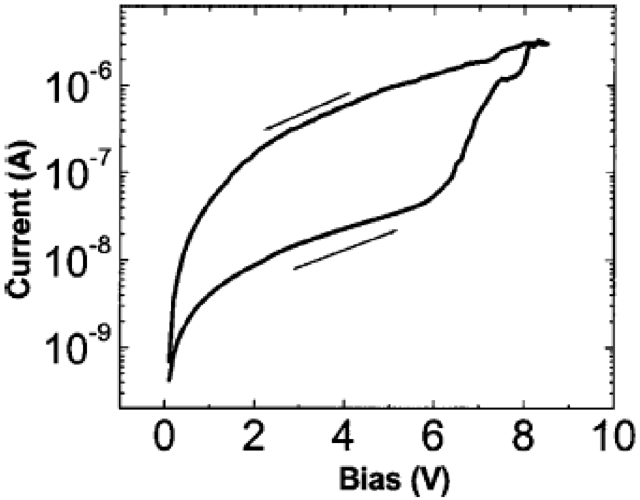
ON/OFF ratio: 10^3

Charge transfer between Au-NP and capping 2NT

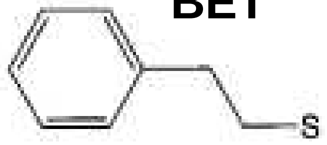


Appl Phys Lett **2005**, *86*, 123507; *Proc IEEE* **2005**, *93*, 1287

Al/Au-BET NP+PS/Al (WORM memory)



BET



Charge transfer between Au-NP and capping BET

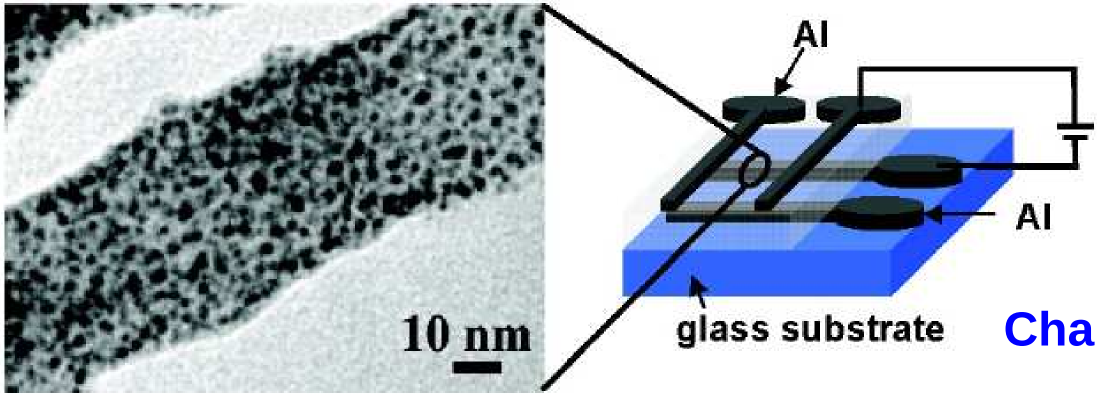
The current at 2V was different two orders in magnitude due to less conjugated π-electrons on BET

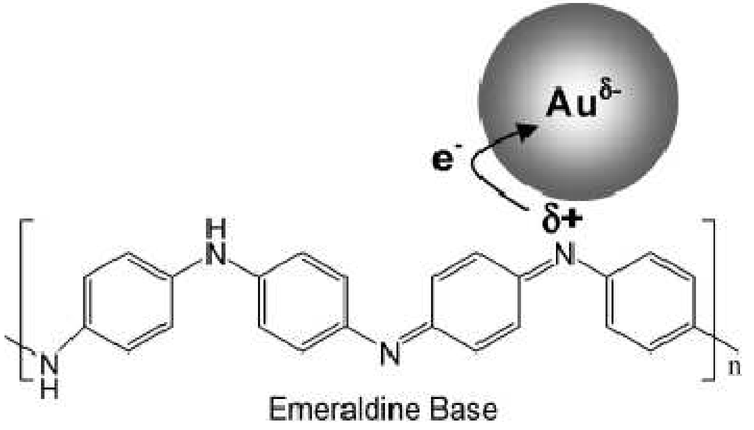
Proc IEEE **2005**, *93*, 1287

Resistor-type Memory: Charge Transfer Effect

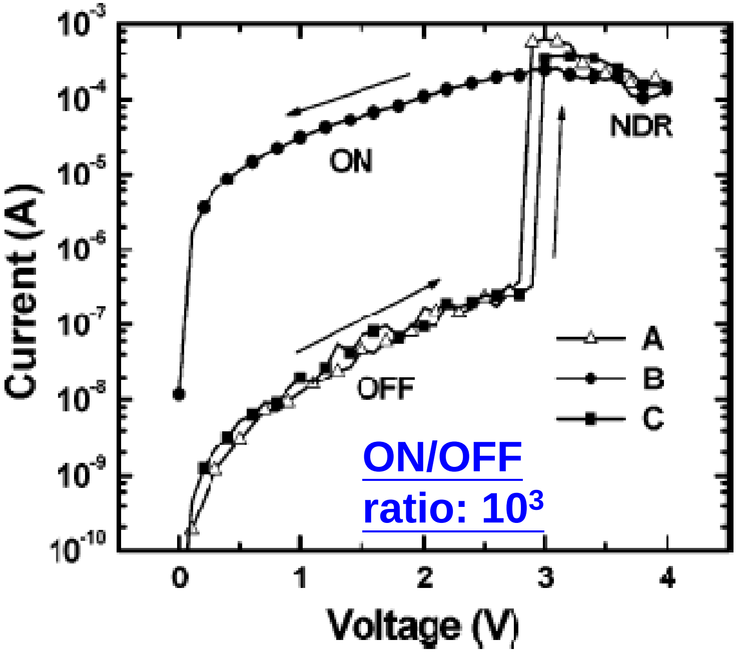
Al/AUNP-PANI nanofiber/Al (flash memory)

1 nm NP within 30 nm diameter PANI fiber

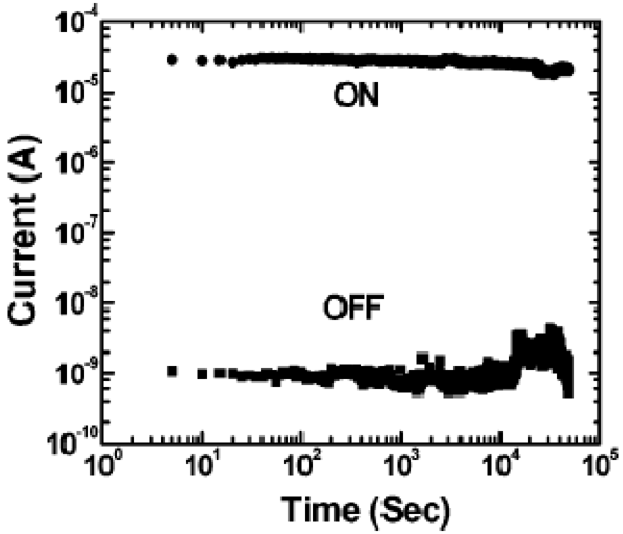




Charge transfer between Au and PANI



ON/OFF ratio: 10^3

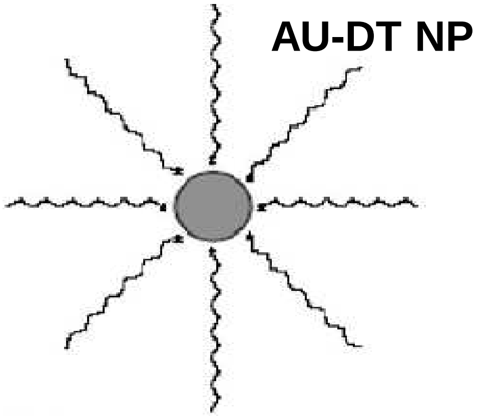


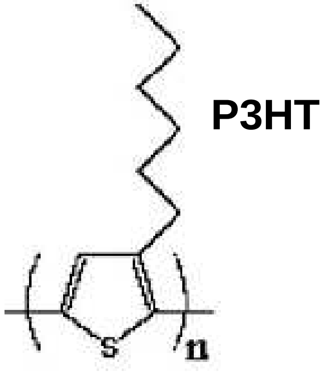
No significant change in conductivity during 14 h stress test

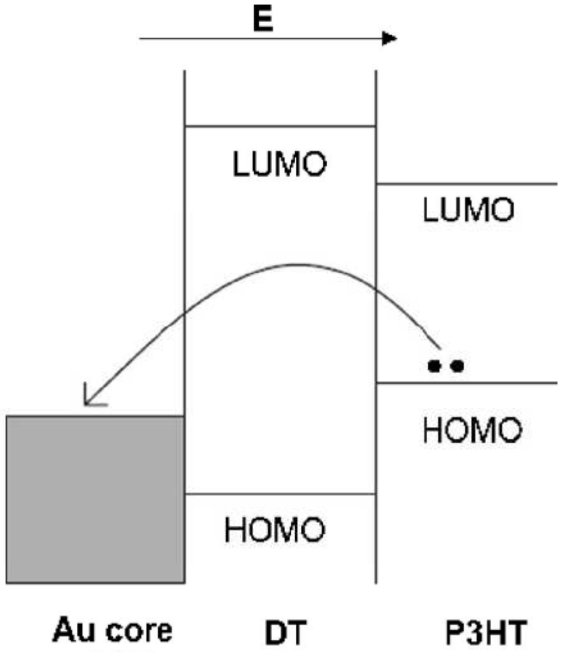
Nano Lett **2005**, *5*, 1077

Resistor-type Memory: Charge Transfer Effect

Al/Au-DT NP+P3HT/Al

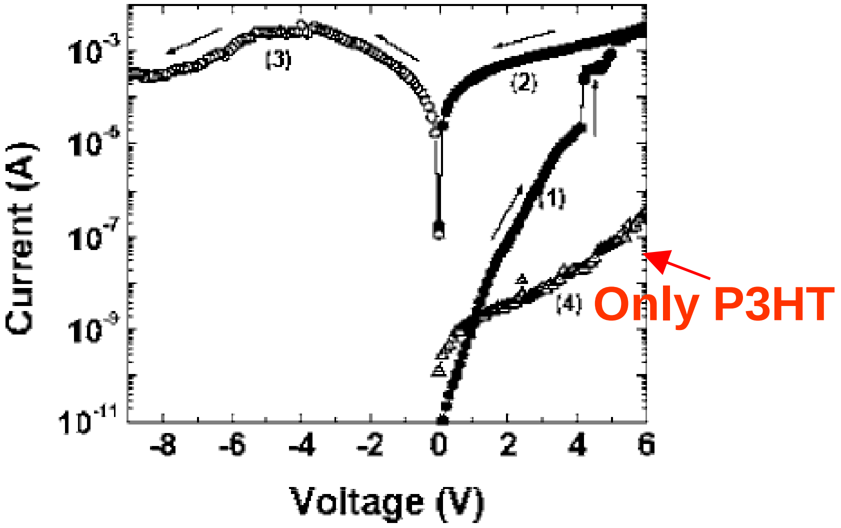


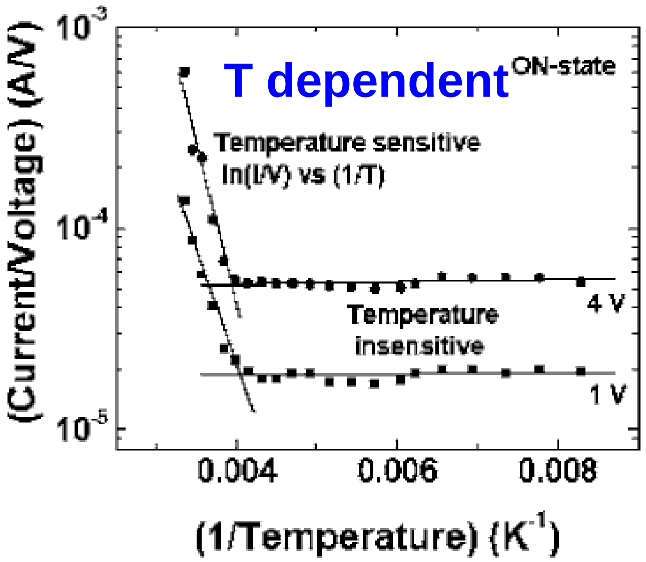




Charge transfer between Au-NP and P3HT

Higher or no erasing voltage is related to the stability of charges in a conjugated polymers



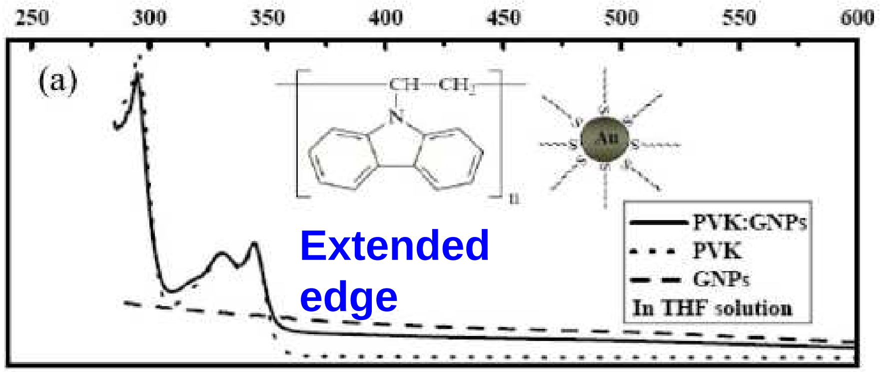


J Appl Phys **2006**, *100*, 54309

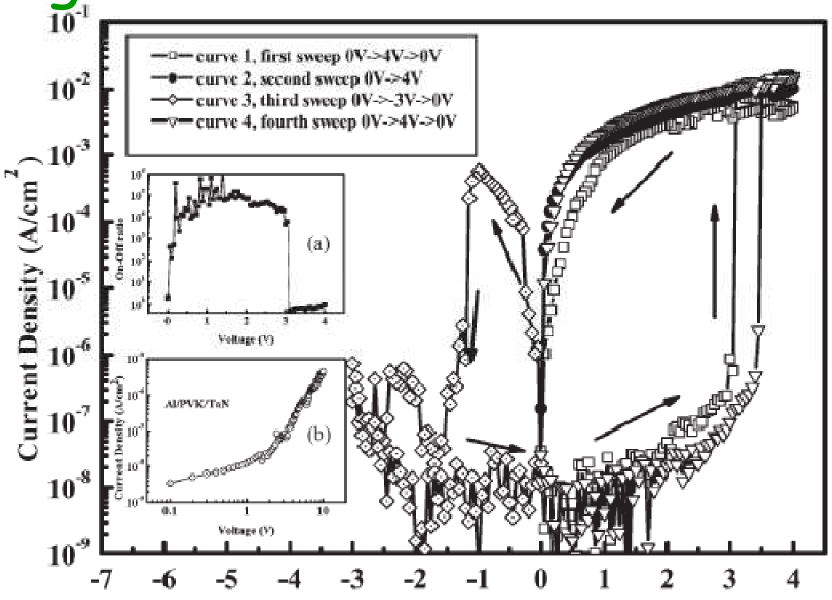
Resistor-type Memory: Charge Transfer Effect

Al/Au-DT NP+PVK/Al (Flash memory)

Absorption spectrum

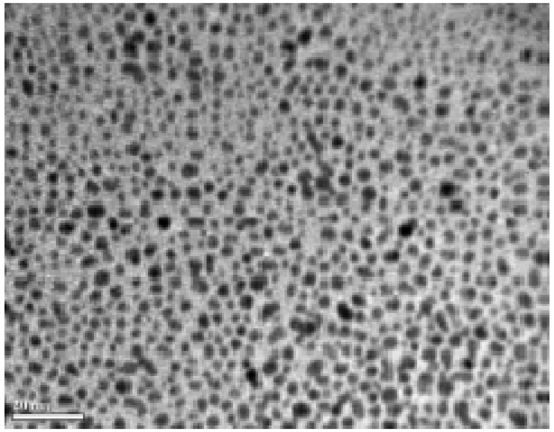


Extended edge

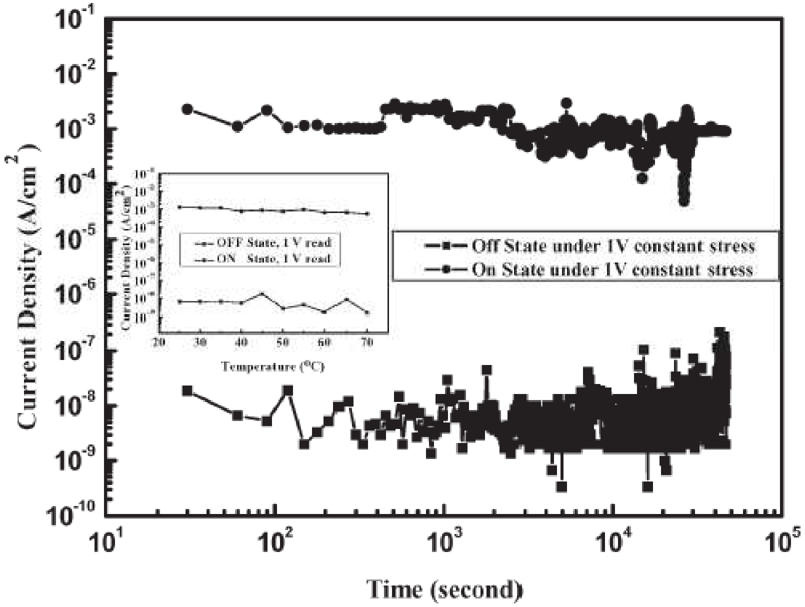


ON/OFF ratio: 10^5

Charge transfer complex between PVK (positively charged) and Au NP (negatively charged) will be formed



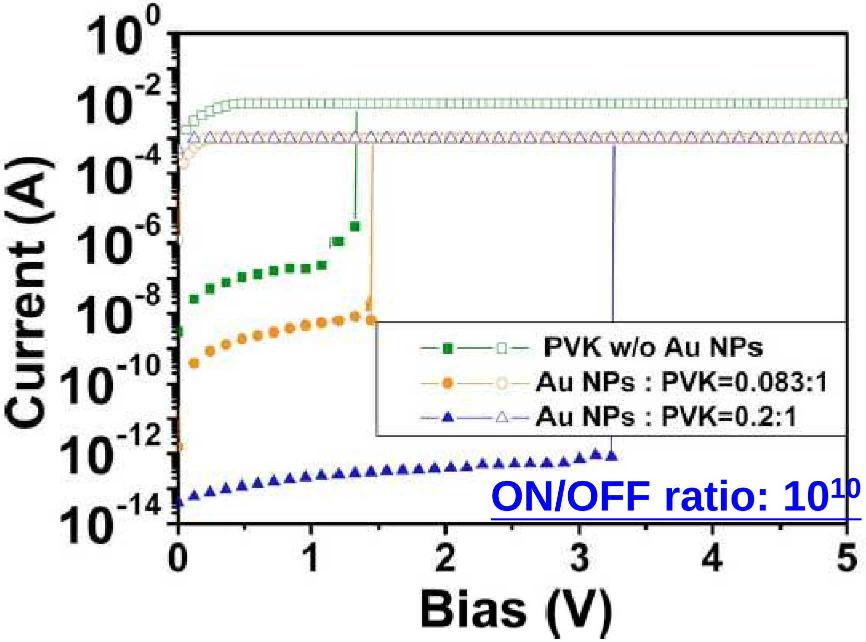
1.5-6.5 nm of Au NP



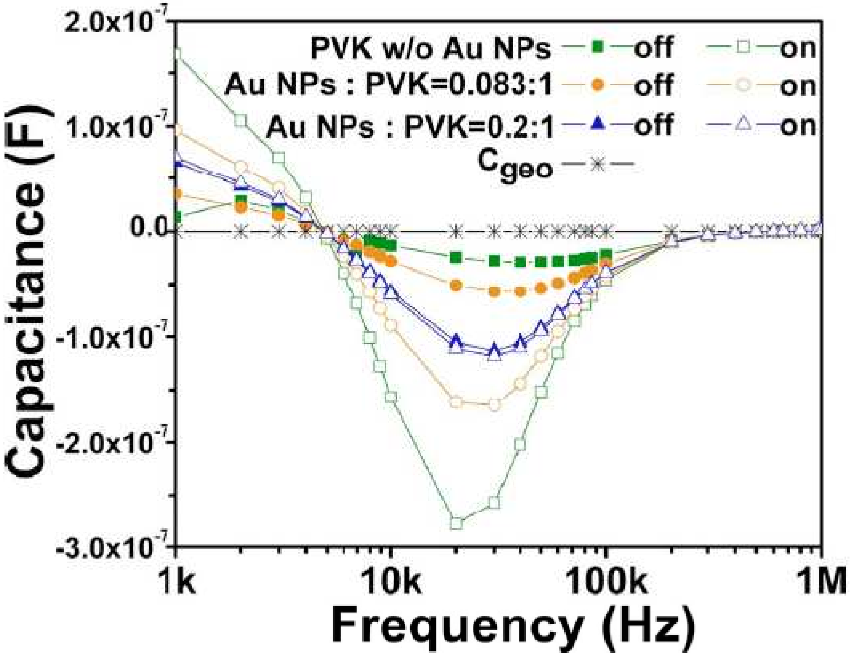
IEEE Electron Device Lett **2007**, *28*, 107

Resistor-type Memory: Charge Transfer Effect

Al/Au-DT NP+PVK/Al



ON/OFF ratio: 10^{10}

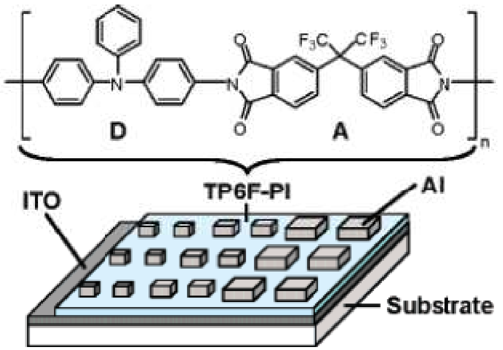


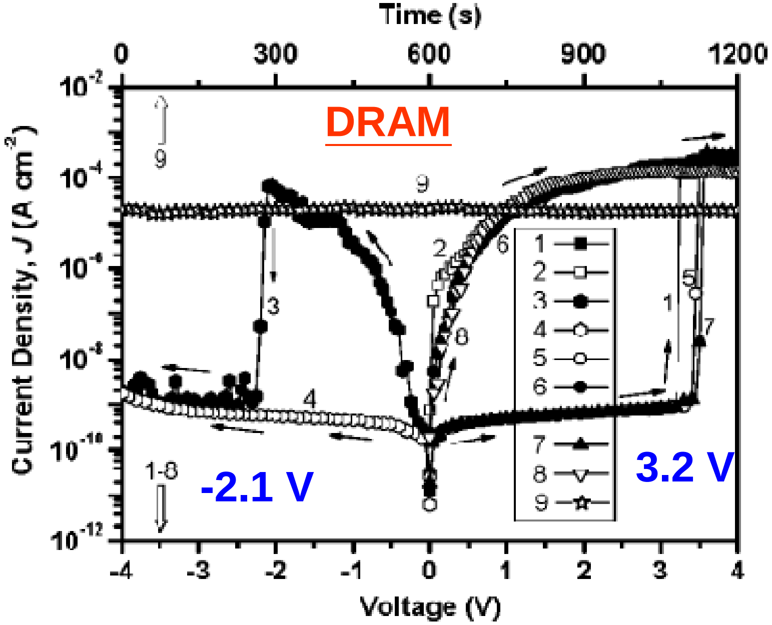
When the carbazole groups of PVK donate electron to Au NPs that at as deeper charge trapping acceptor under bias, the carbazole and Au NPs are charged positively and negatively.

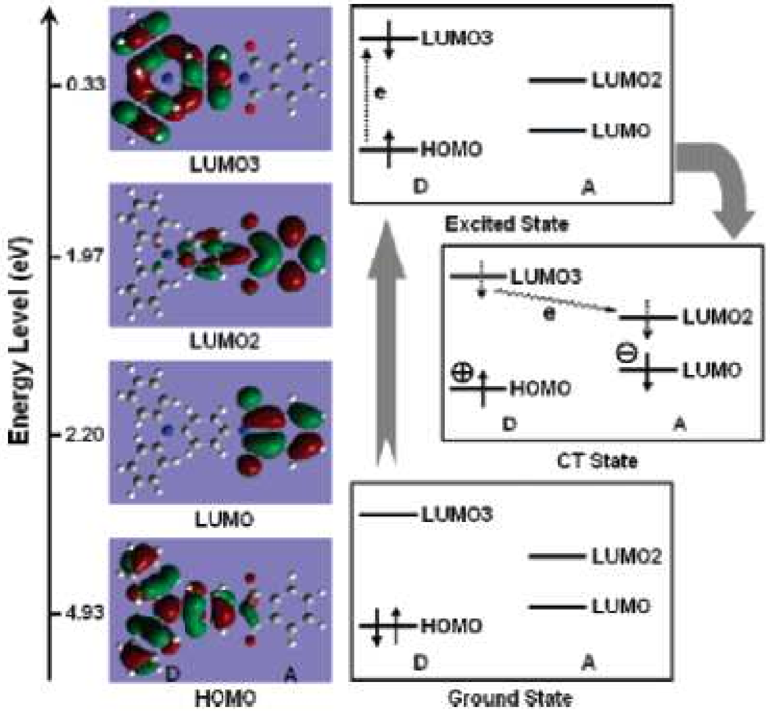
C-F curves reveals that carrier transport is dominated by hopping of hole of PVK, rather than leaping of carriers through Au NPs. Au NPs prevent the holes from bring recombined by defect so the peaks of C-F curves become deeper with increasing Au NP ratio.

Appl Phys Lett **2008**, *93*, 153305

Resistor-type Memory: Charge Transfer Effect





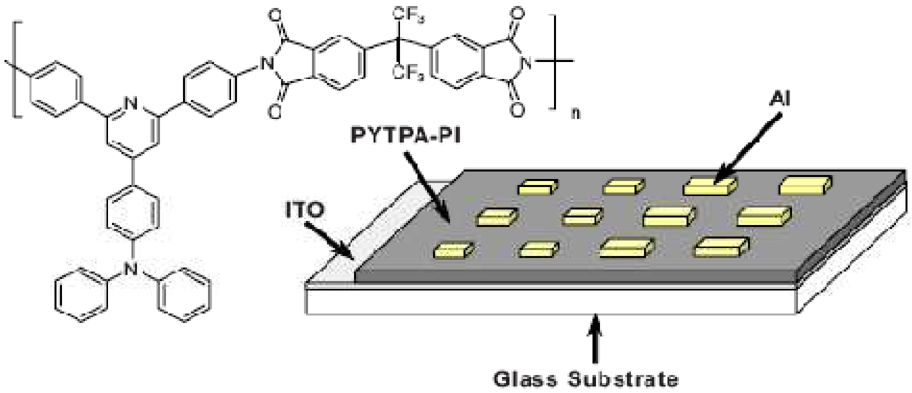


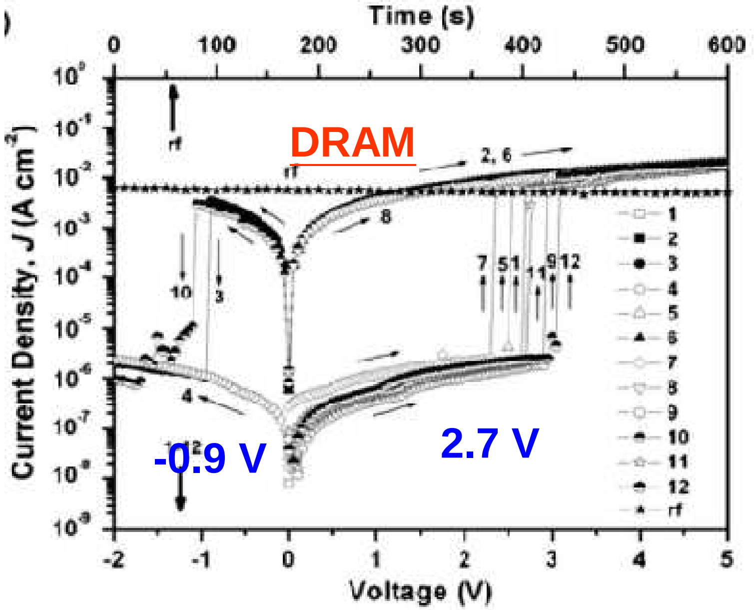
At the Vt, on electron transits from HOMO to LUMO3 within D to from excited state. CT can occur indirectly from HOMO to LUMO2, then to LUMO of A or directly from HOMO to LUMO2 and LUMO at the excited state to from a conductive CT complex

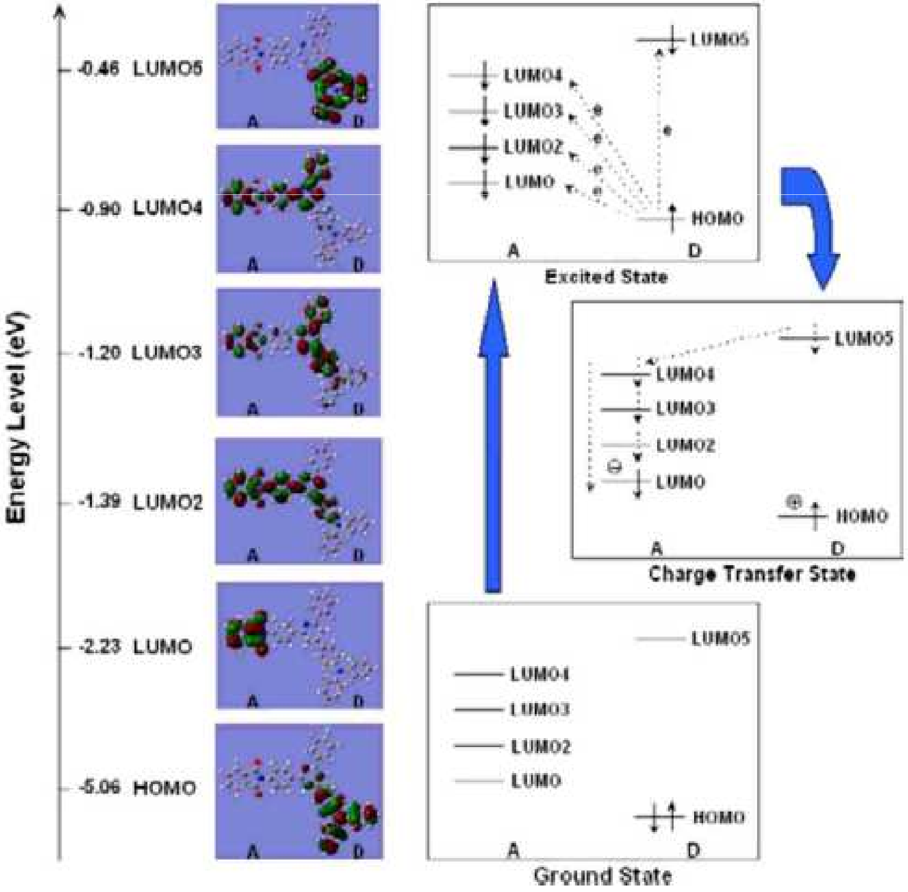
The lower HOMO explain the higher switch ON voltage while smaller dipole moment (2.06D) leads to a more stable CT structure

J Am Chem Soc **2006**, *127*, 8733

Resistor-type Memory: Charge Transfer Effect







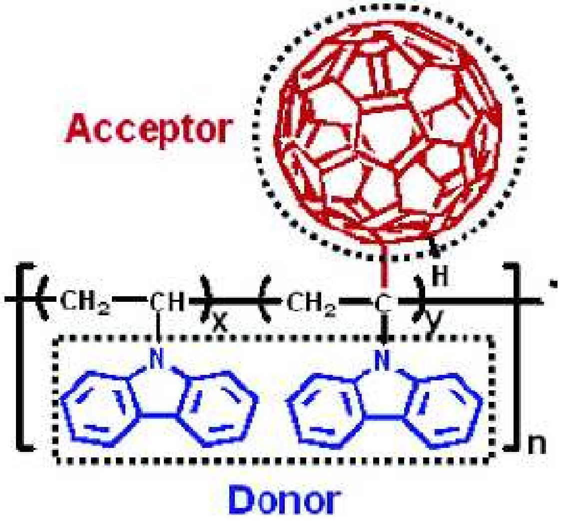
Some electrons at HOMO transit to LUMO5 of TPA to give rise to an excited state. Electron at HOMO are also excited to intermediate LUMOs due to overlapping of the HOMO and intermediate LUMOs at PhPy and TPA. Charge transfer : indirectly from LUMO5 to the intermediate LUMOs and the LUMO or from intermediate LUMOs to LUMO or directly from HOMO to LUMO.

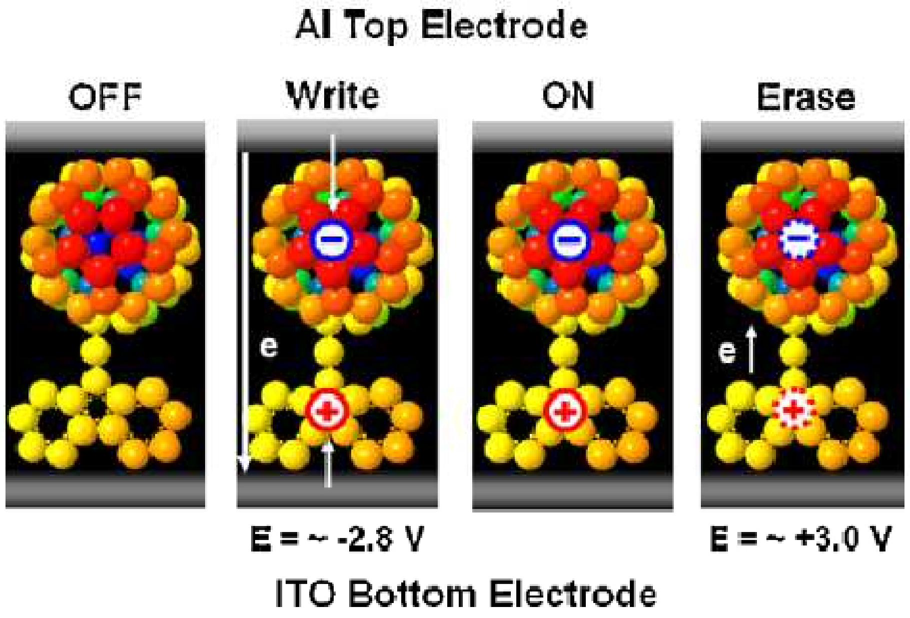
Dipole moment is 2.55 D indicating that the polarity is not strong enough to retain the charge transfer state.

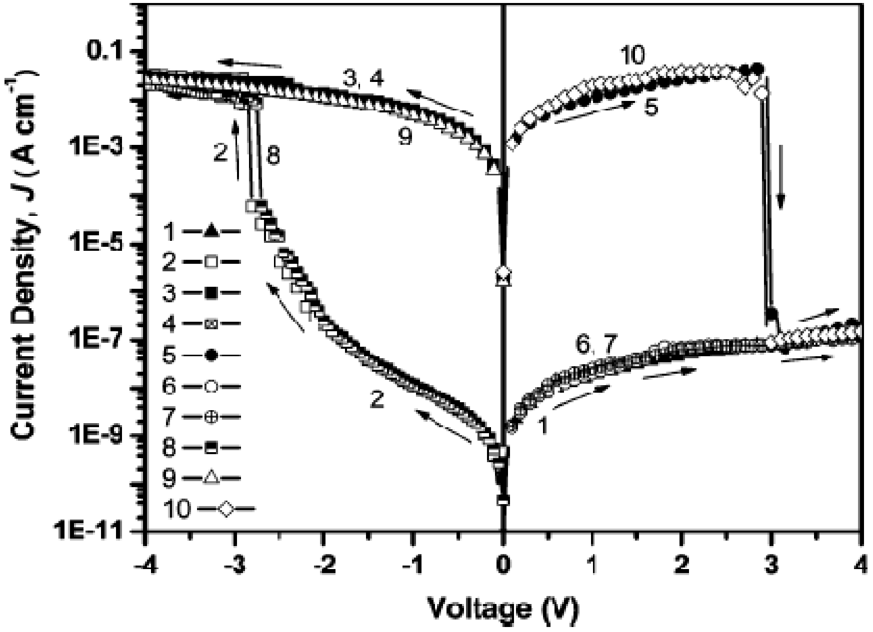
J Appl Phys **2009**, *105*, 044501

Resistor-type Memory: Charge Transfer Effect

ITO/PVK-C_{60}/Al (flash memory)







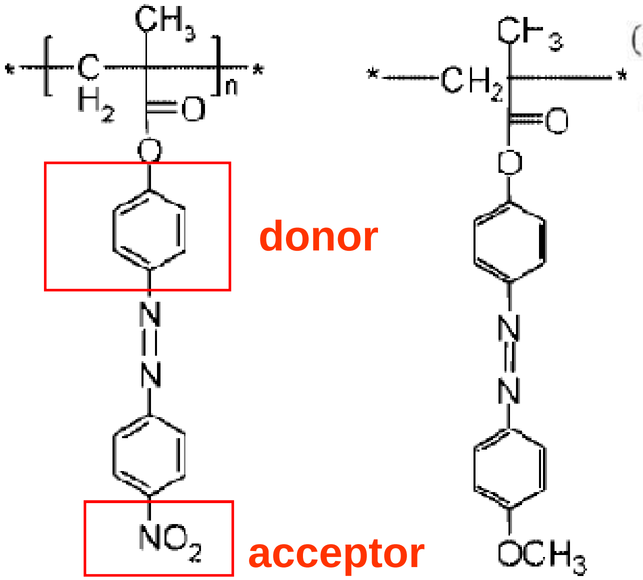
When the electric field exceeds the energy barriers between PCK-C_{60} and electrode, holes are injected into HOMO of Cz and electrons are injected into LUMO of C_{60}. The charged HOMO of Cz and LUMO of C_{60} form a channel for charge carriers through CT interaction.

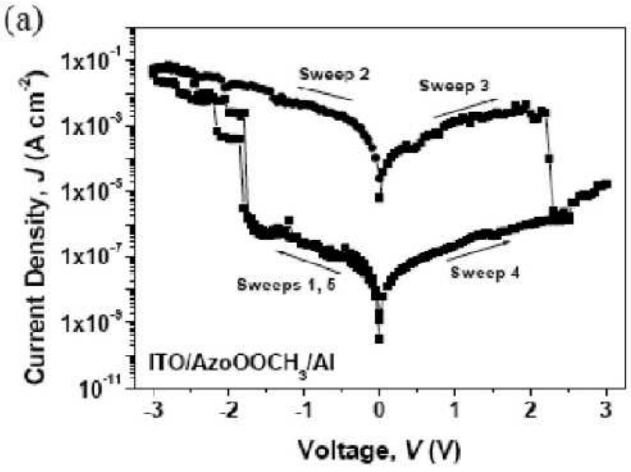
Under a reverse bias, C_{60} loses the charged state to neutralize the positively charge Cz moiety

Langmuir **2007**, *23*, 312

Resistor-type Memory: Intramolecular CT Effect

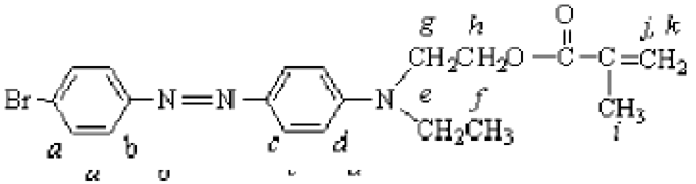
AzoONO$_2$(flash) **AzoOOCH$_3$ (WORM)**



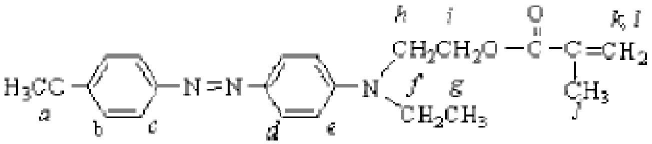


ON/OFF ratio: 10^4-10^6

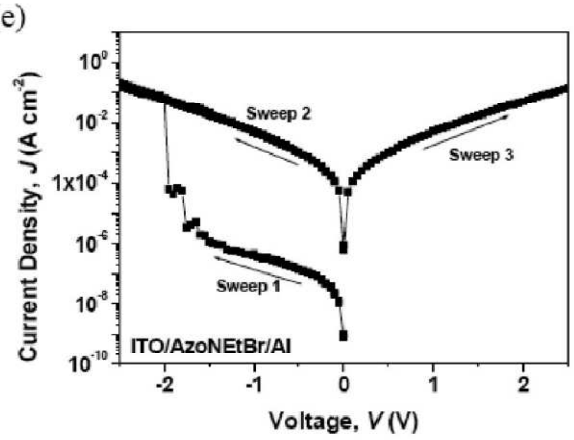
When the terminal moieties of azobenzene chromophore are acceptors, trapped charges are stabilized by ICT from a charge separated state. The filled traps may be easily detrapped under reverse bias, resulting in a high conductivity state for a long time in nitro and bormo containing azobenzene.



AzoNErBr (flash)



AzoNEtOCH$_3$ (WORM)



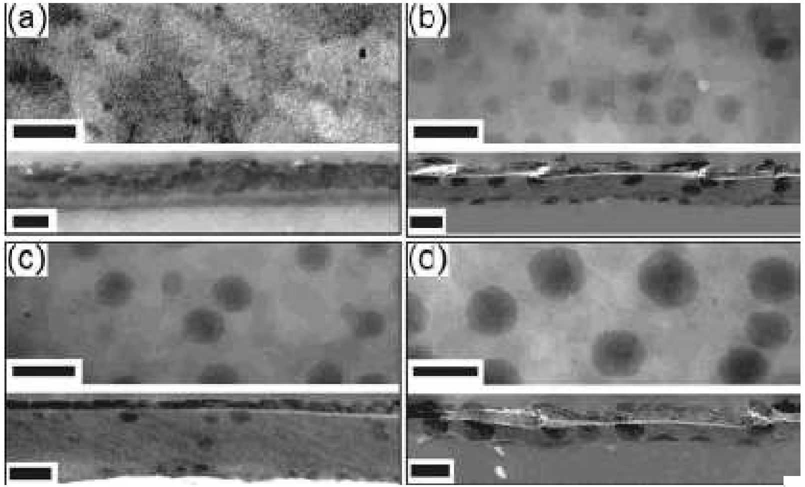
Azobenzene chromophore containing donor are not able to undergo ICT state and the trapped charges can be detrapped by reverse bias

ACS Appl Mater & Interface **2009**, *1*, 60

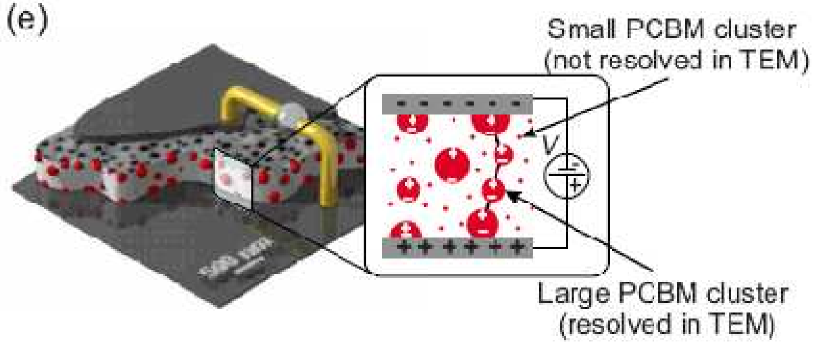
Resistor-type Memory

Al/PS+PCBM/Al

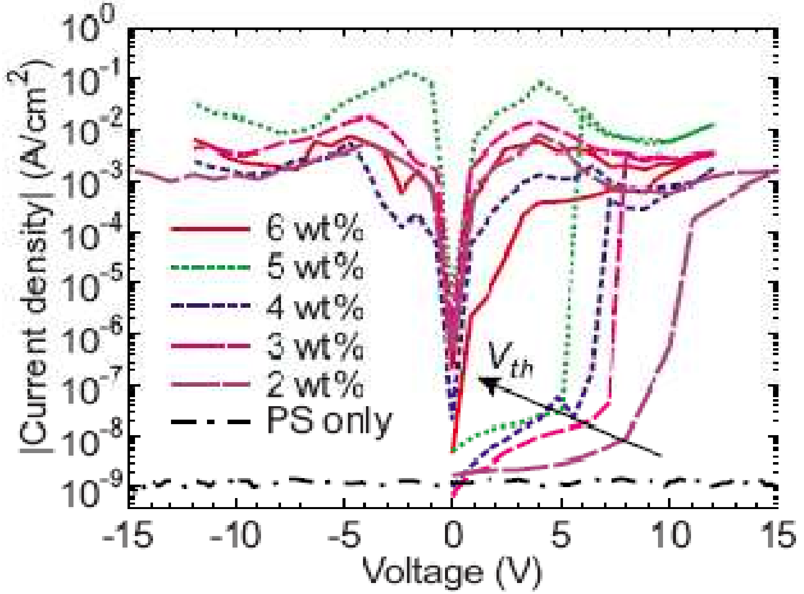
5% PCBM **10% PCBM**

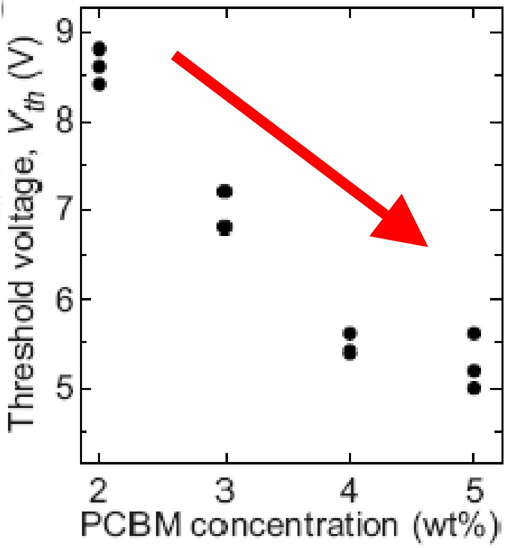


20% PCBM **40% PCBM**



polarization between PCBM cluster separated by PS matrix.



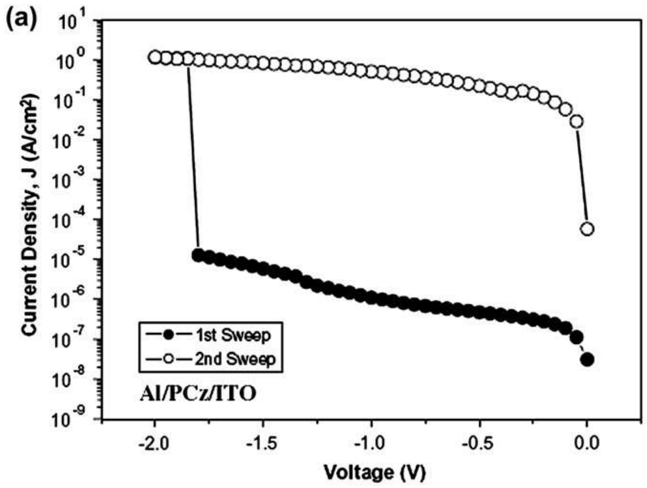


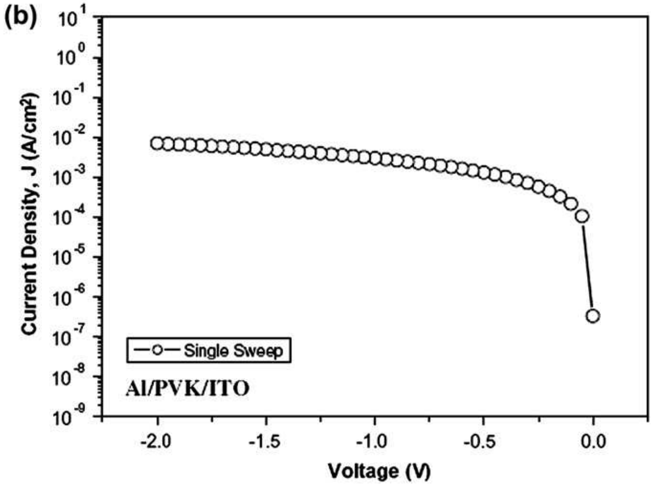
Vth suggests to result from the polarization of PCBM cluster and generation of a stronger electrical field between the adjacent cluster.

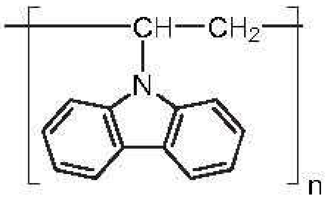
High PCBM concentration leads to short circuit due to the formation of cluster chain or single large cluster.

Appl Phys Lett **2008**, *92*, 253308

Resistor-type Memory: Conformational Effects

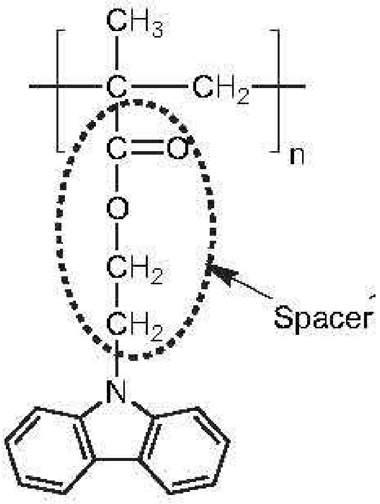






PVK

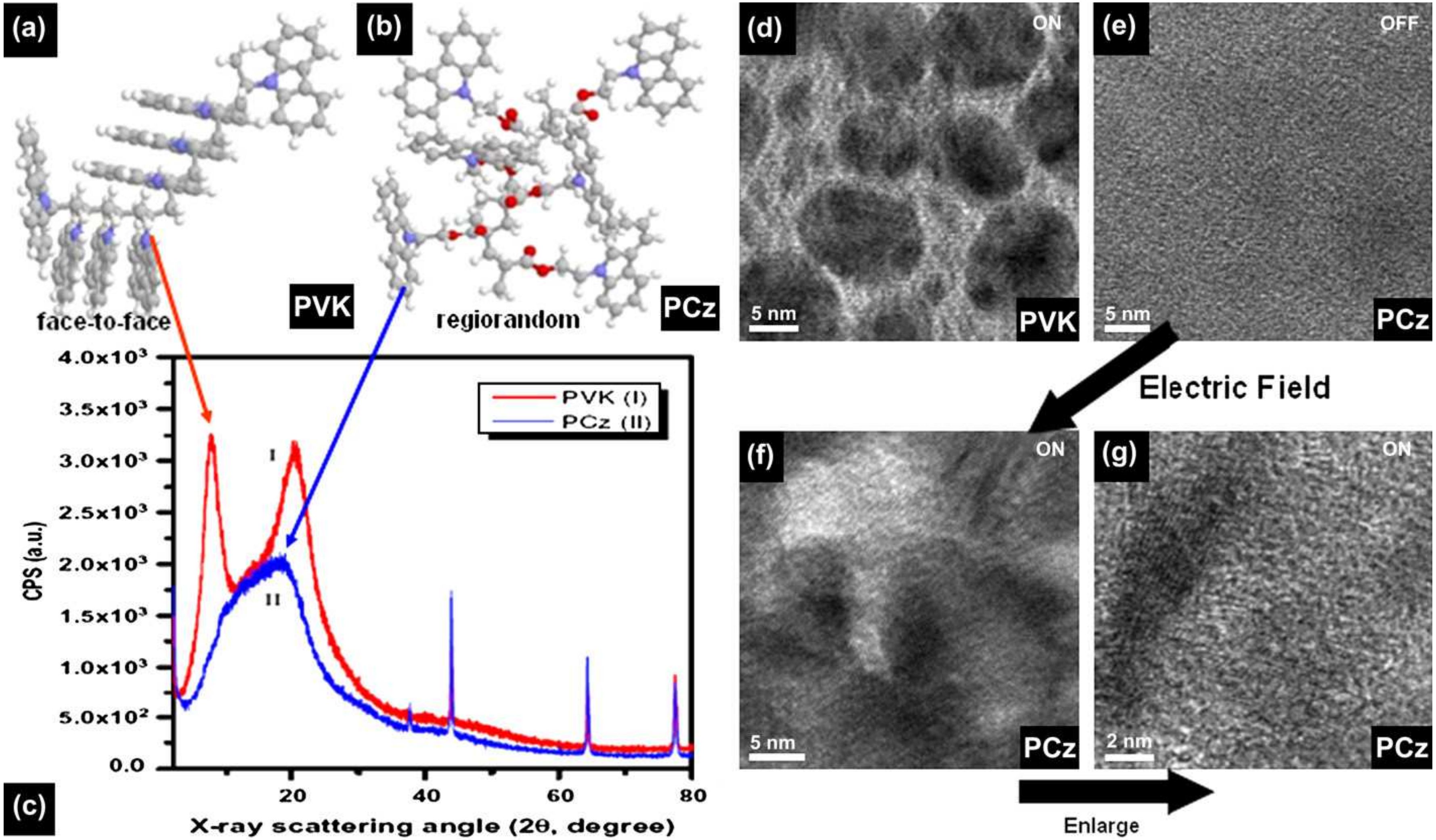
Regiorandom structure



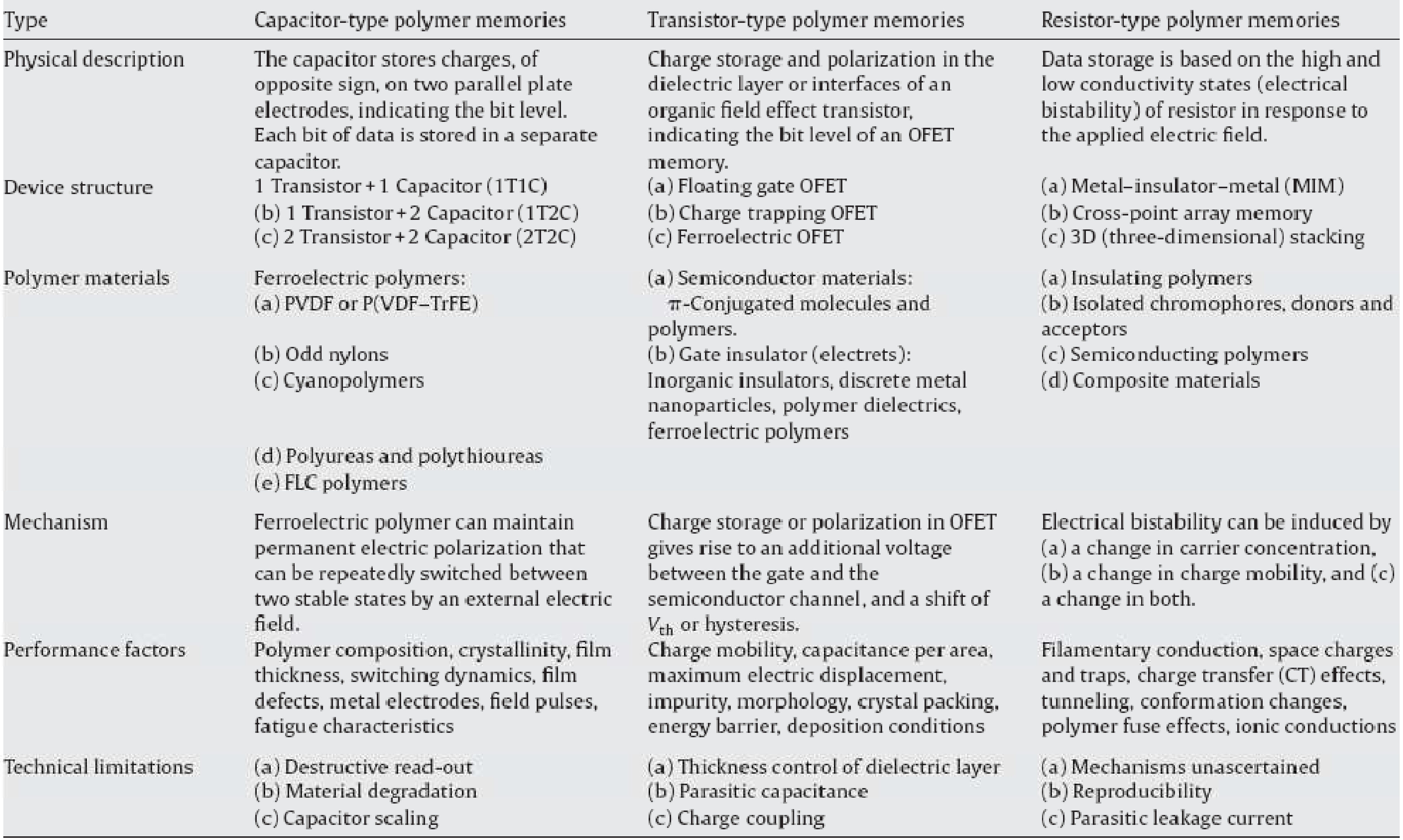
PCz

Face-to-face regioregular structure

Resistor-type Memory: Conformational Effects

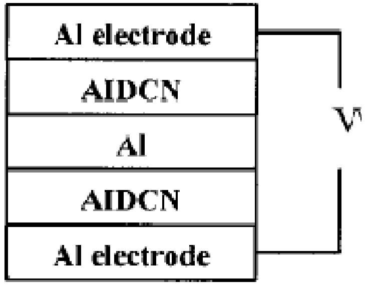


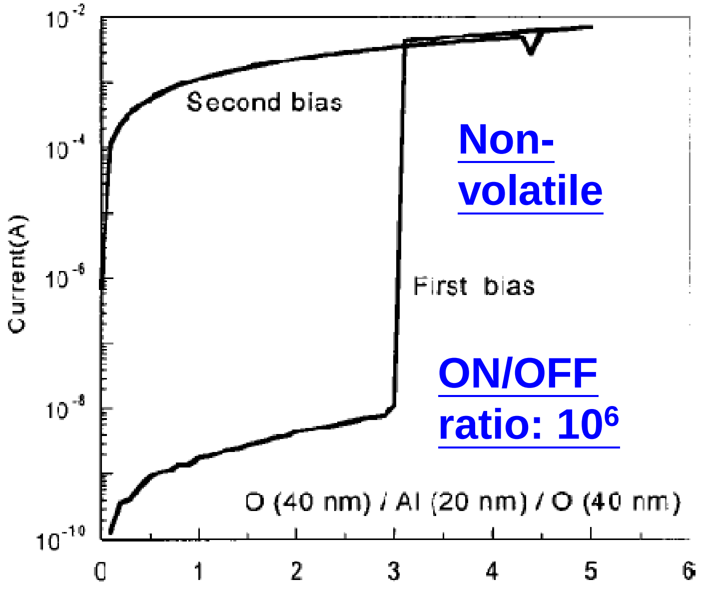
Comparison of the Three Types of Polymer Memory Classified by Primary Circuit Elements



Type	Capacitor-type polymer memories	Transistor-type polymer memories	Resistor-type polymer memories
Physical description	The capacitor stores charges, of opposite sign, on two parallel plate electrodes, indicating the bit level. Each bit of data is stored in a separate capacitor.	Charge storage and polarization in the dielectric layer or interfaces of an organic field effect transistor, indicating the bit level of an OFET memory.	Data storage is based on the high and low conductivity states (electrical bistability) of resistor in response to the applied electric field.
Device structure	1 Transistor + 1 Capacitor (1T1C) (b) 1 Transistor + 2 Capacitor (1T2C) (c) 2 Transistor + 2 Capacitor (2T2C)	(a) Floating gate OFET (b) Charge trapping OFET (c) Ferroelectric OFET	(a) Metal–insulator–metal (MIM) (b) Cross-point array memory (c) 3D (three-dimensional) stacking
Polymer materials	Ferroelectric polymers: (a) PVDF or P(VDF–TrFE) (b) Odd nylons (c) Cyanopolymers (d) Polyureas and polythioureas (e) FLC polymers	(a) Semiconductor materials: π-Conjugated molecules and polymers. (b) Gate insulator (electrets): Inorganic insulators, discrete metal nanoparticles, polymer dielectrics, ferroelectric polymers	(a) Insulating polymers (b) Isolated chromophores, donors and acceptors (c) Semiconducting polymers (d) Composite materials
Mechanism	Ferroelectric polymer can maintain permanent electric polarization that can be repeatedly switched between two stable states by an external electric field.	Charge storage or polarization in OFET gives rise to an additional voltage between the gate and the semiconductor channel, and a shift of V_{th} or hysteresis.	Electrical bistability can be induced by (a) a change in carrier concentration, (b) a change in charge mobility, and (c) a change in both.
Performance factors	Polymer composition, crystallinity, film thickness, switching dynamics, film defects, metal electrodes, field pulses, fatigue characteristics	Charge mobility, capacitance per area, maximum electric displacement, impurity, morphology, crystal packing, energy barrier, deposition conditions	Filamentary conduction, space charges and traps, charge transfer (CT) effects, tunneling, conformation changes, polymer fuse effects, ionic conductions
Technical limitations	(a) Destructive read-out (b) Material degradation (c) Capacitor scaling	(a) Thickness control of dielectric layer (b) Parasitic capacitance (c) Charge coupling	(a) Mechanisms unascertained (b) Reproducibility (c) Parasitic leakage current

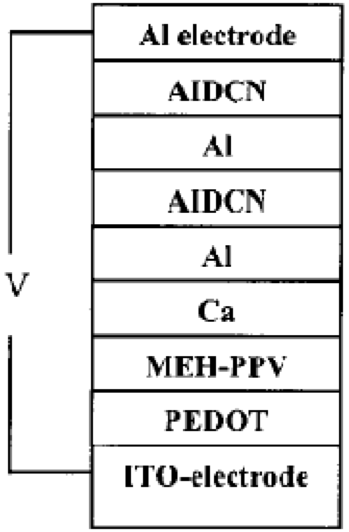
Organic Bistable Light-Emitting Devices

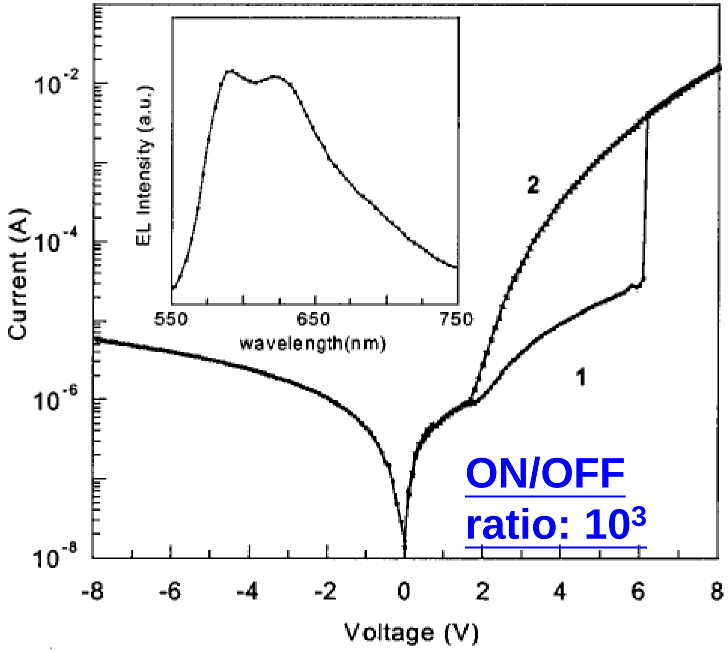




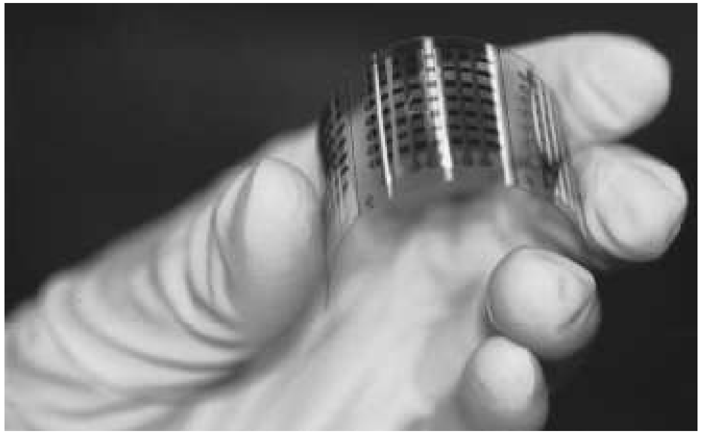
Non-volatile

ON/OFF ratio: 10^6





ON/OFF ratio: 10^3



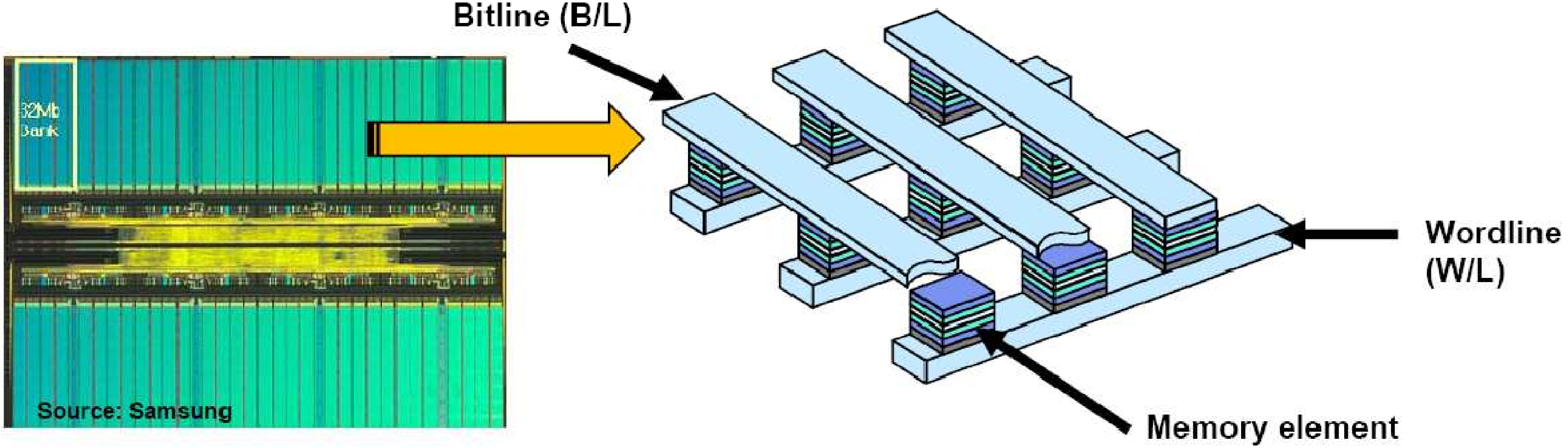
Memory array on a regular plastic overhead transparency

EL spectrum with the brightness 280 cd/m^2 at 3mA

Further application on digital memory, opto-electronic books and recordable paper

Appl Phys Lett **2002**, *80*, 362

Recent Effect: Cross-Point Memory



Source: Samsung

Requirement

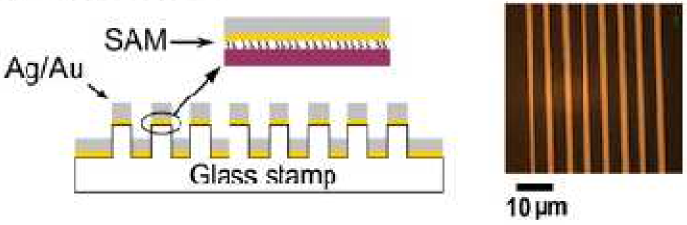
- Stackable, low temperature processing
- Enough current drive for programming
- Unidirectional and ideally bidirectional programming

Resistor-type Memory: SCLC and Filament Formation

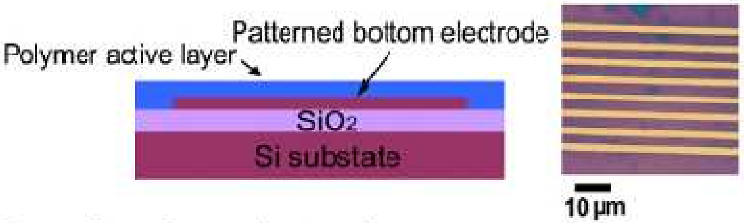
Cross bar type polymer non-volatile memory

Direct metal transfer (DMT)

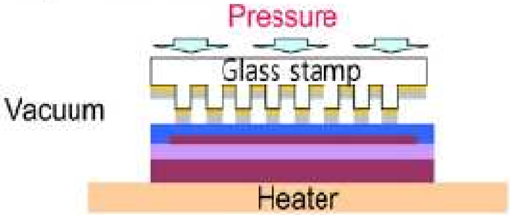
(a) Metal evaporation



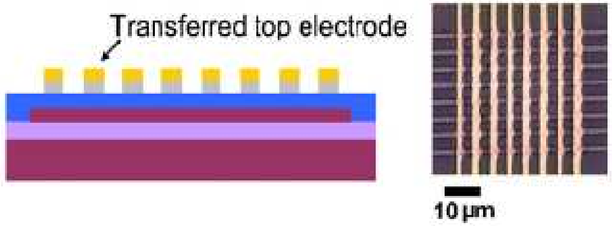
(b) Spin-coating polymer film

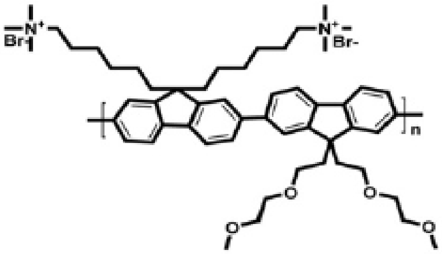


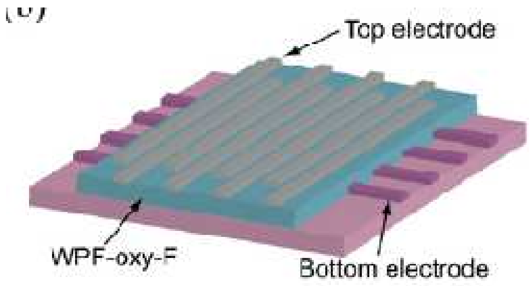
(c) Transfer of top electrode

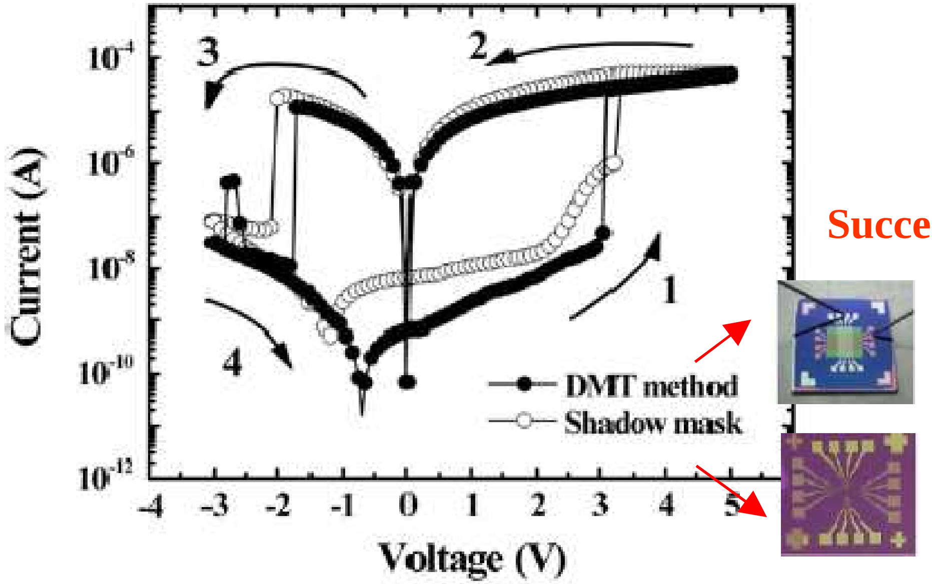


(d) Detaching stamp









Successful

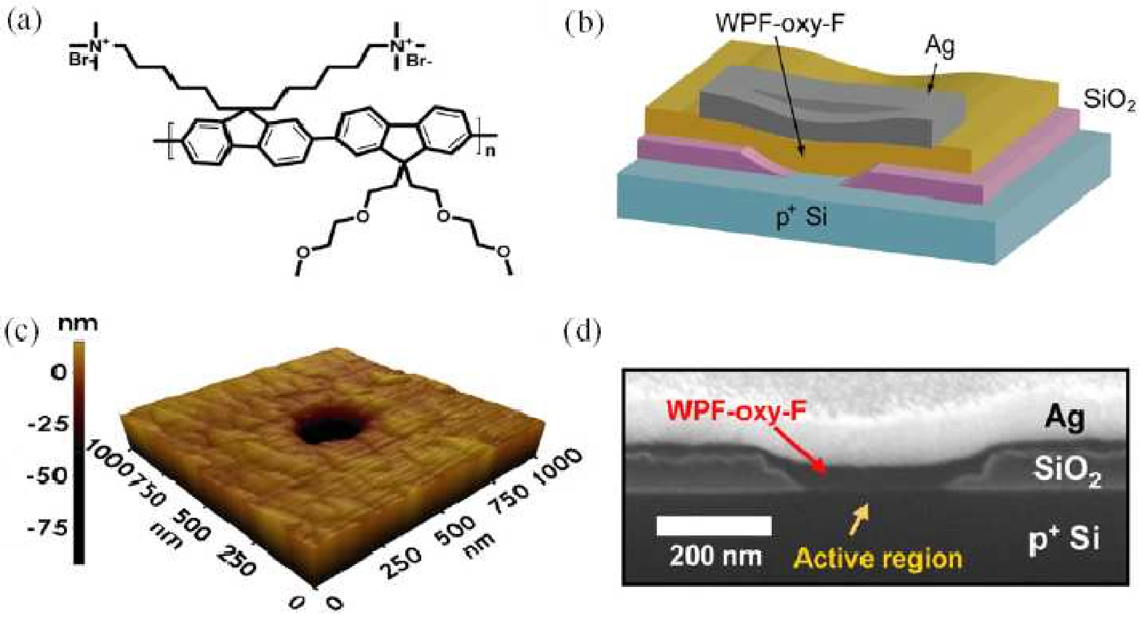
64 %

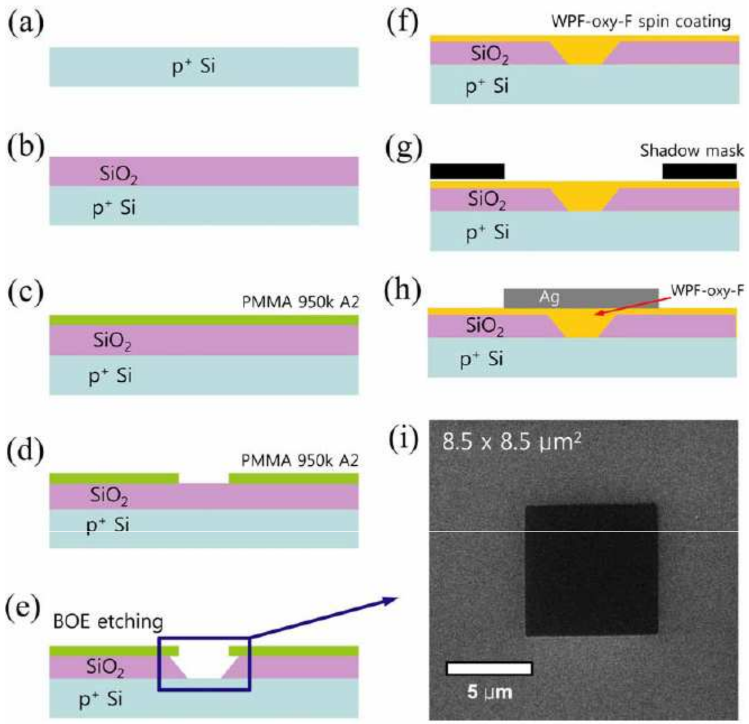
90 %

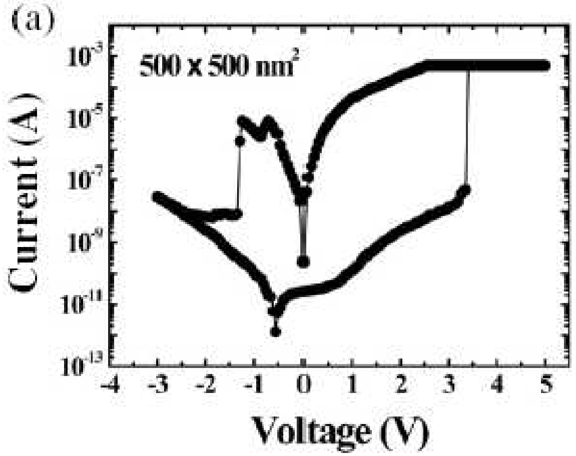
Nanotechnology **2008**, *19*, 405201

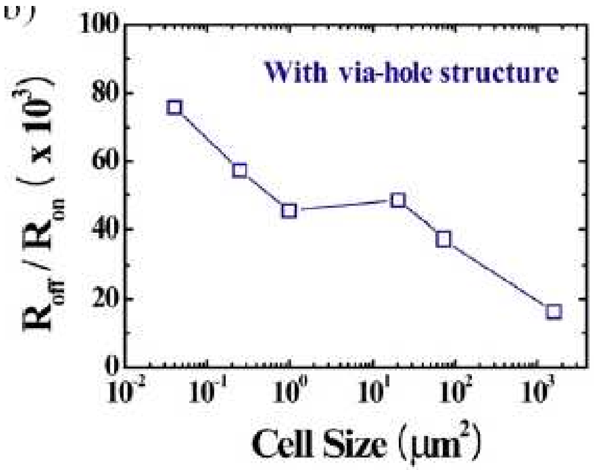
Resistor-type Memory: SCLC and Filament Formation

Polymer non-volatile memory in a scalable via-hole structure







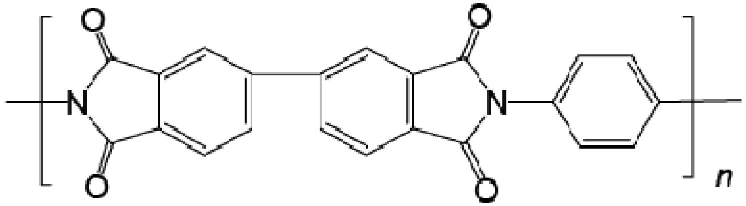


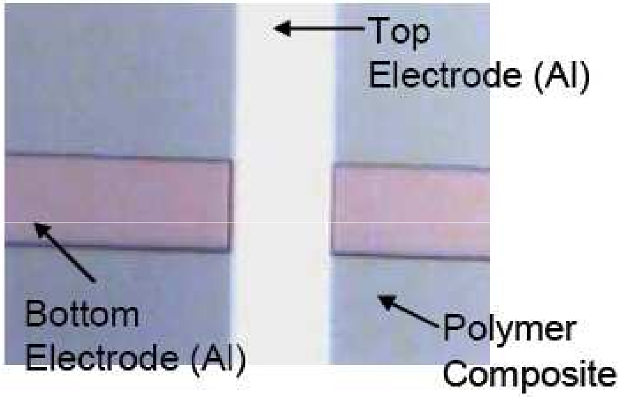
Polymer memory device varying from micron scale to sub-micro scale were produced using an e-beam lithography technique

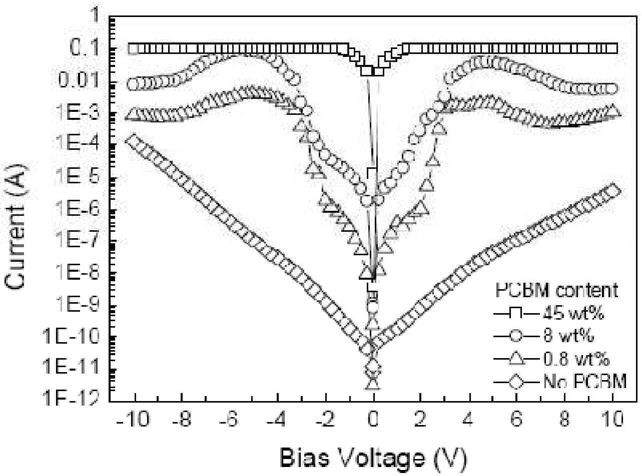
Nanotechnology **2009**, *20*, 025201

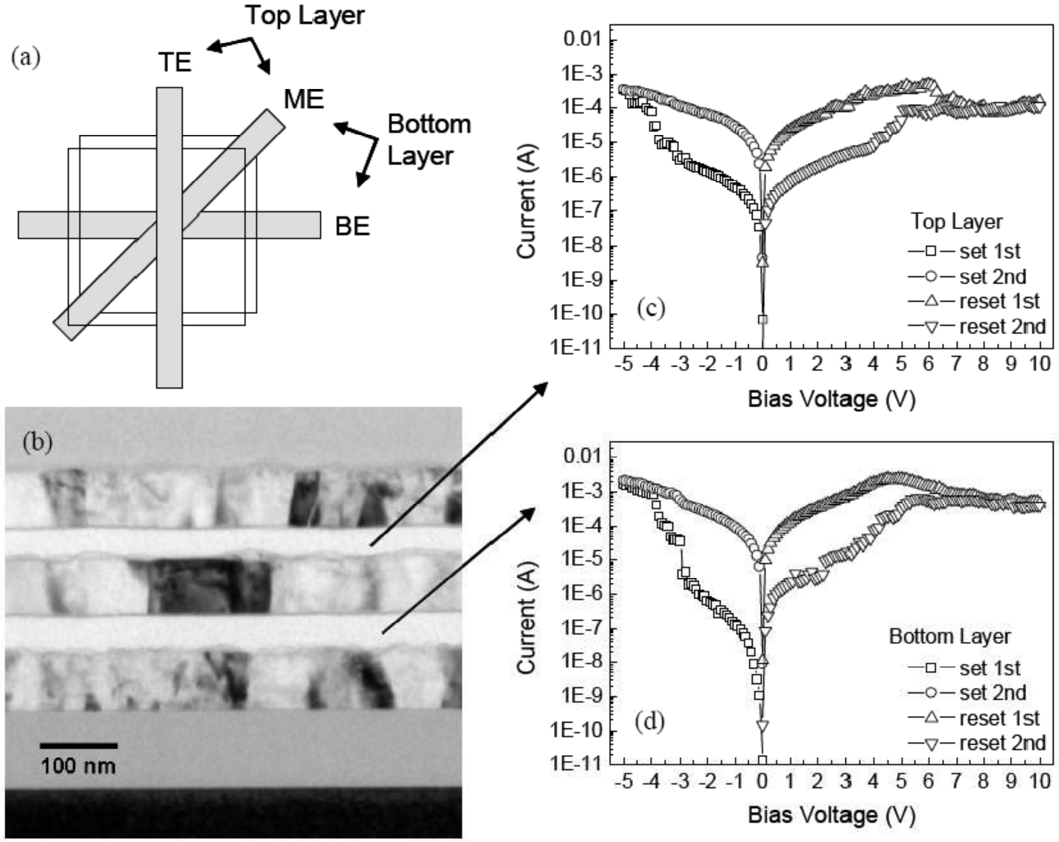
Multilayer Resistor-type Memory

Al/PI+PCBM/Al (flash memory)







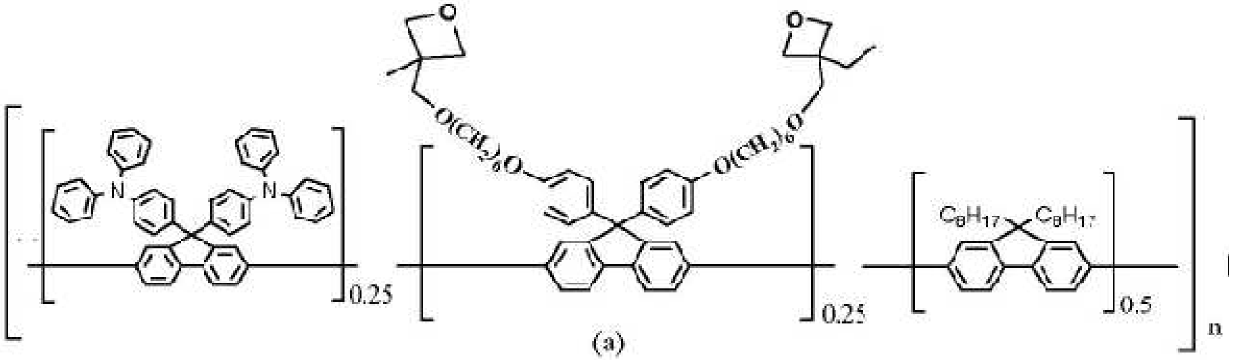


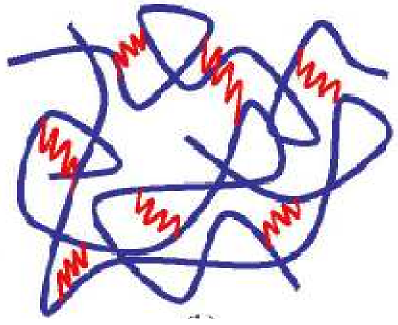
The PI:PCBM memory device is thermally robust and adequate for multi layer stacking.

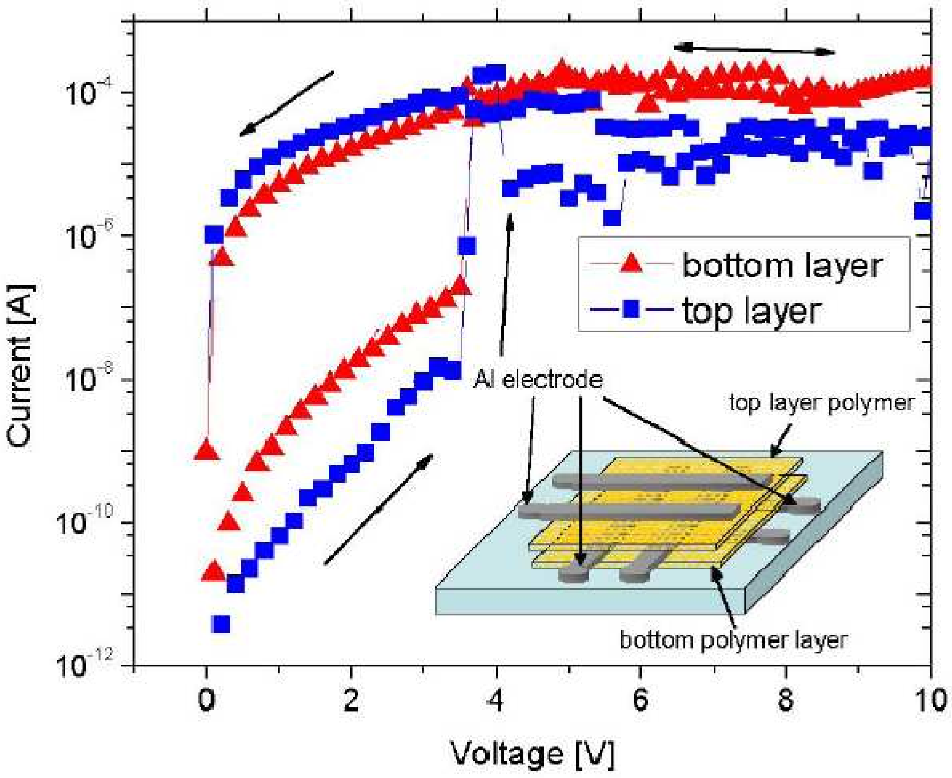
The ON state is achieved by electron paths provided by LUMO of PCBM.

IEDM **2005**

Stacked Resistive Memory Device Using Photo Cross-linkable Copolymer







Due to its robustness achieved through the cross-linking process, multi-level stacking of the device is possible and it is compatible with conventional photolithographic process

Since all the functional groups are included in a copolymer system, the problem of phase separation is also eliminated.

IEDM **2006**, 237

Conclusions

- New Materials enable new memory devices
  - Plenty of new materials, difficult to satisfy memory requirements
- Scalability is a key issue
  - Stackable, small cell size, multi-bit/cell
- New read / write / endurance characteristics enable new circuit/system design

H. S. Philips Wong, “*Emerging Memories*” 2008

Big company have groups working on organic memory devices!