Polymer Electronic Memories: Materials, Devices and Mechanisms

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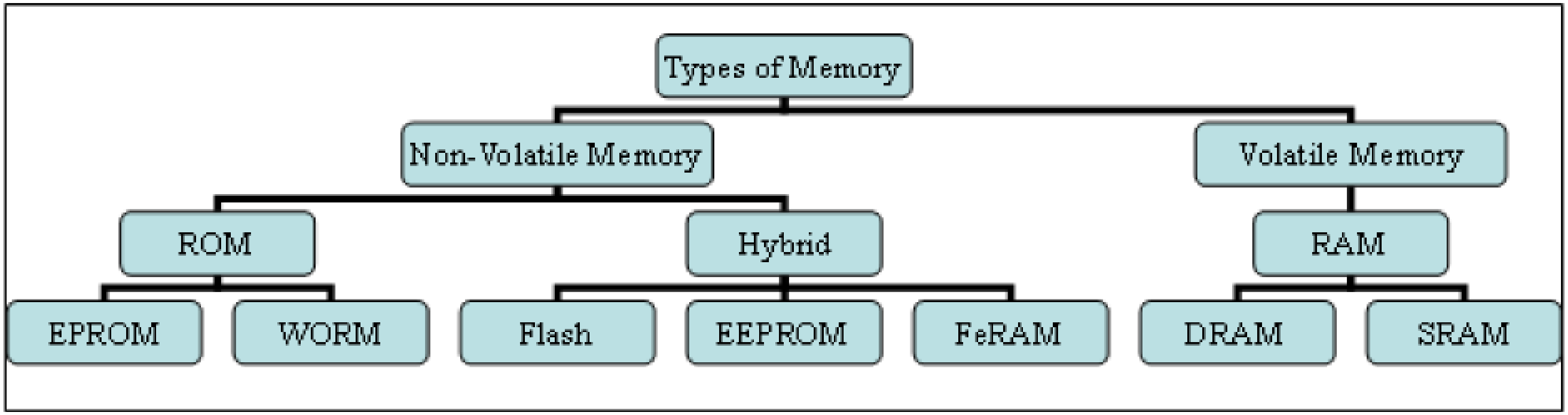
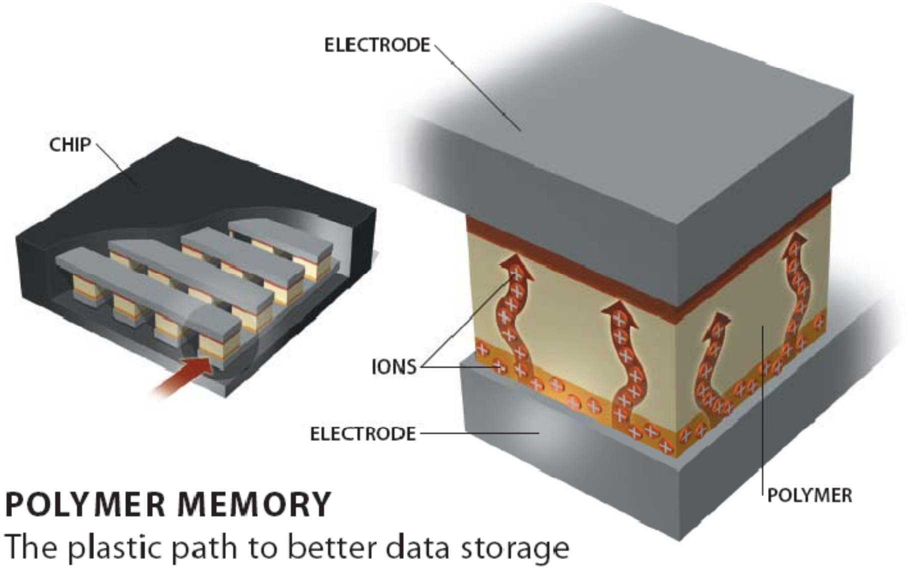
Polymer and Molecular Memories

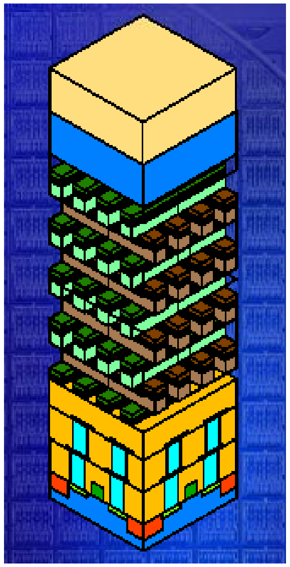


ROM: Read Only Memory
EPROM: Electrically Programmable Read-Only Memory
WORM: Write-Once Read-Many-Times
Flash: Rewritable
EEPROM: Electrically Erasable Programmable Read-Only Memory
FeRAM: Ferroelectric Random Access Memory
RAM: Random Access Memory
DRAM: Dynamic Random Access Memory
SRAM: Static Random Access Memory

Stimuli-Responsive Polymers for Information Storage

Rather than encoding "0" and "1" as the amount of charge stored in a Si cell, a polymer memory stores data in another form, for instance, based on the high and low conductivity response to an applied voltage (electrical bistability)





Multi-layer construction

A. Stikeman, Technol Rev 2002 105 31

Classification of Polymer Memories

Mechanistic Analogy Between the Polymer Memory Elements and the 3 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	(a) 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, tunnelling, 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

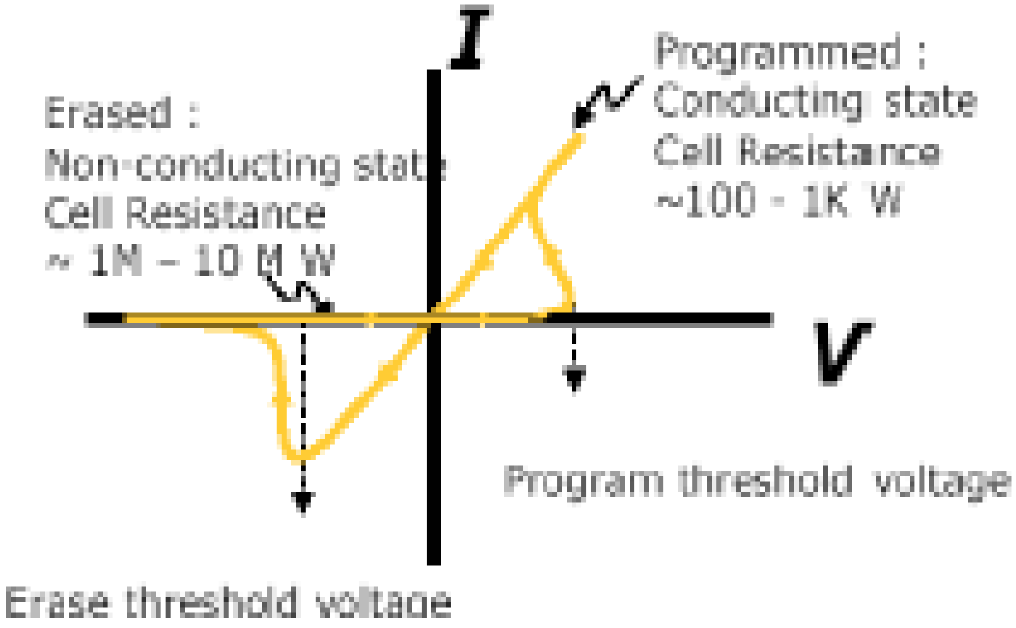
Prog Polym Sci 2008 33 917-978

Resistive Random Access Memory (RRAM)

Data Storage Based on Electrical Bistability (ON- and OFF-states) of Materials Arising from Changes in Intrinsic Properties, e.g., CT, Phase/Conformation Change and Redox, in Response to the Applied Electric Field (not based on a specific cell structure, e.g., FET, or Si CMOS technology)

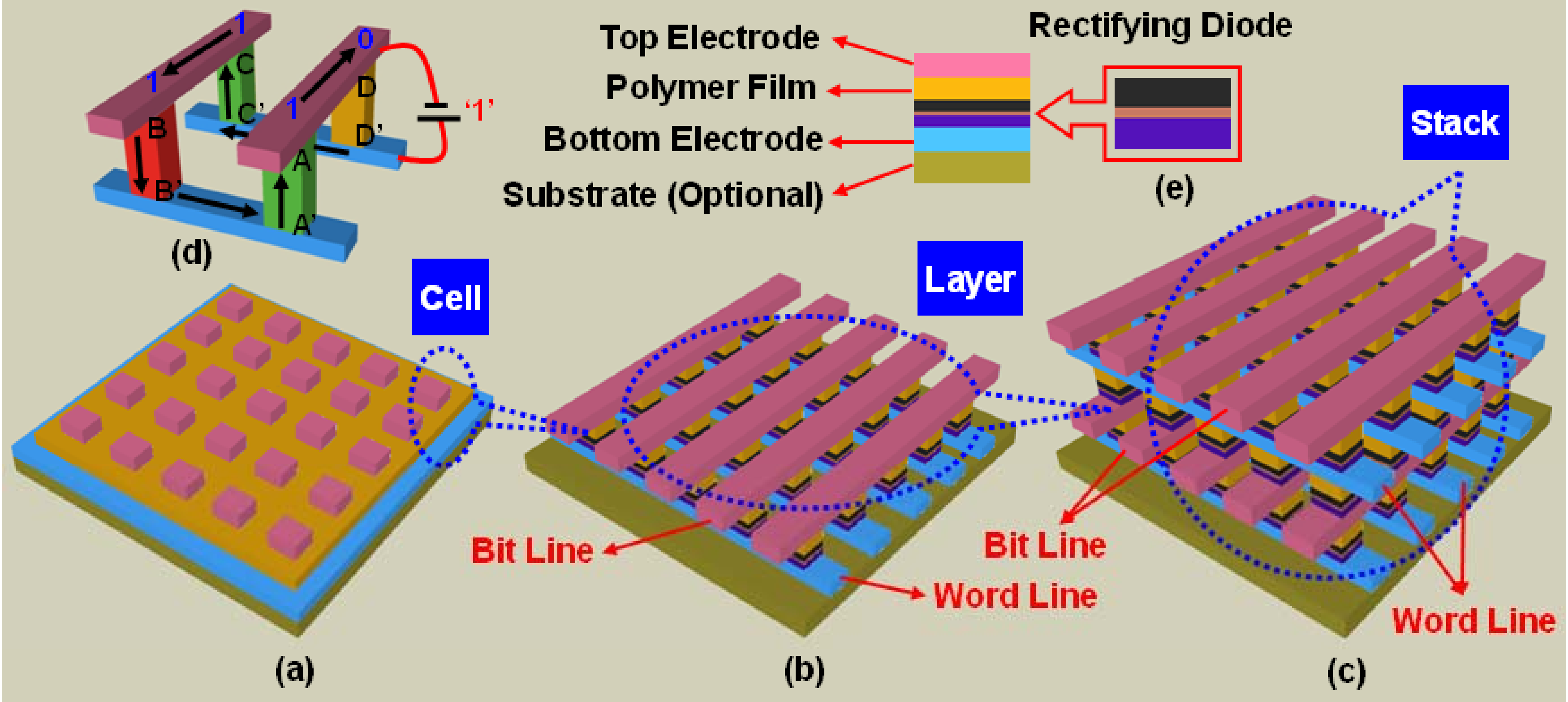
Polymeric material serving as a fuse:

- **-Write a bit with high current (blow the fuse)**
- **-Read a bit with low current (check to see if the fuse is blown)**
- **-Rewritable memories use reversible fuse states**



Resistive Random Access Memory (RRAM)

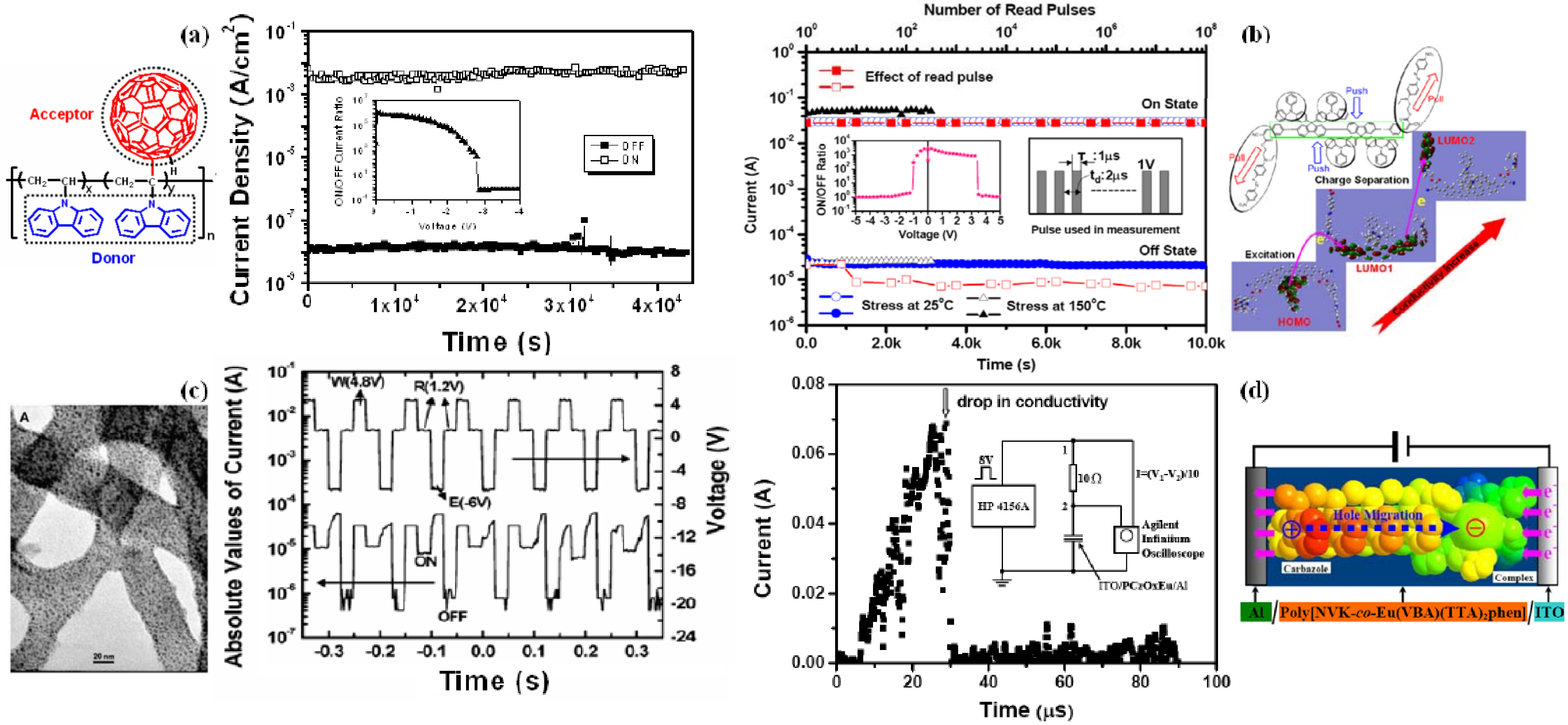
General Device Structures



(a) 5 × 5 testing polymer devices and the basic configuration of a memory cell,
(b) a 5 (Word line) × 5 (Bit line) cross-point memory array,
(c) a 2 (Stacked layer) × 5 (Word line) × 5 (Bit line) stacked memory device,
(d) parasitic paths in cross-point memories, and
(e) rectifying diode integrated to avoid parasitic currents.

Resistive Random Access Memory (RRAM)

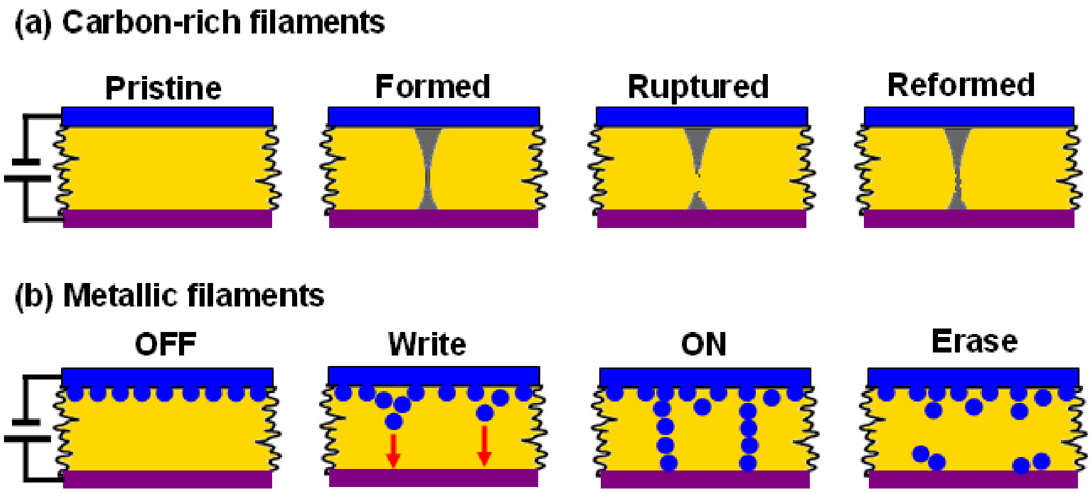
Evaluation parameters for molecular/polymer memories

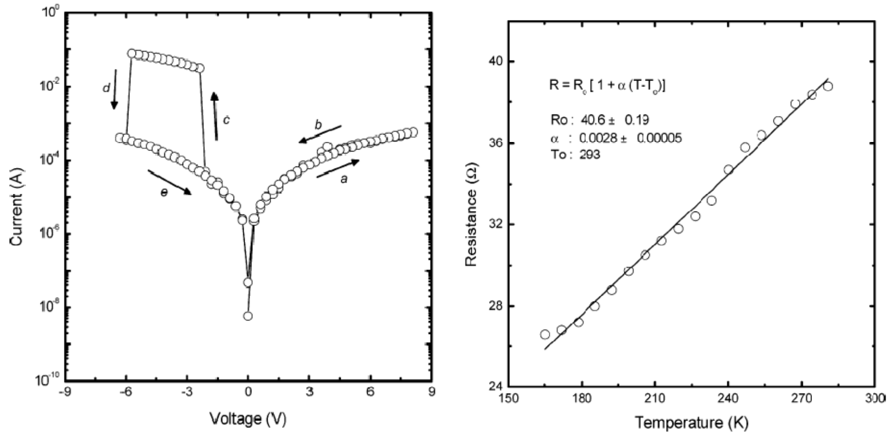


- **(a)** **Stability under voltage stress and ON/OFF ratio (inset)** [PVK-C_{60}, *Langmuir 2007 23 312*]
- **(b)** **Thermal stress and number of read pulses** [Conjugated triad, *Appl Phys Lett 2008 92 143302*]
- **(c)** **Write-read-erase-read (WRER) cycles** [PANi nf-Au np, *Y Yang et al. Nano Lett 2005 5 1077]*
- **(d)** **Switching time measurement** [PVK-Eu copolymer, *Adv Mater 2005 17 455].*

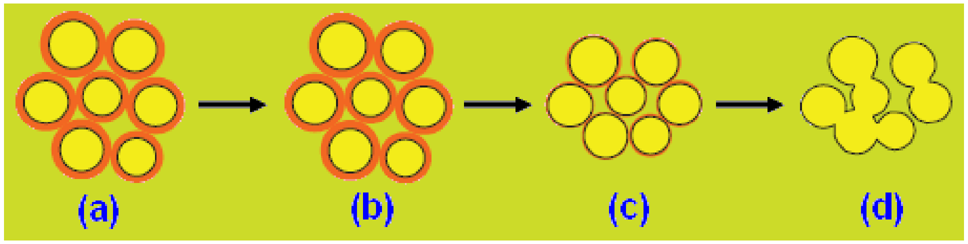
Resistive Random Access Memory (RRAM)

RRAM from Filamentary Conduction

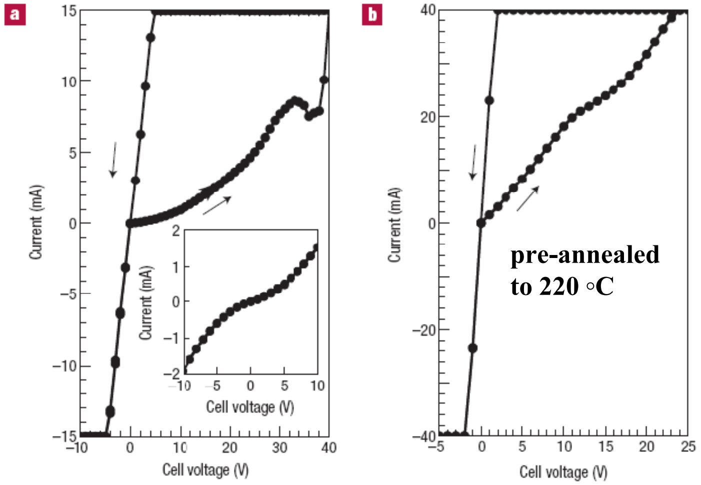




I-V curve and temp-dependent R of regioregular P3HT device attributable to metal filaments [*Joo et al. J Phys Chem B 2006 110 23812*]

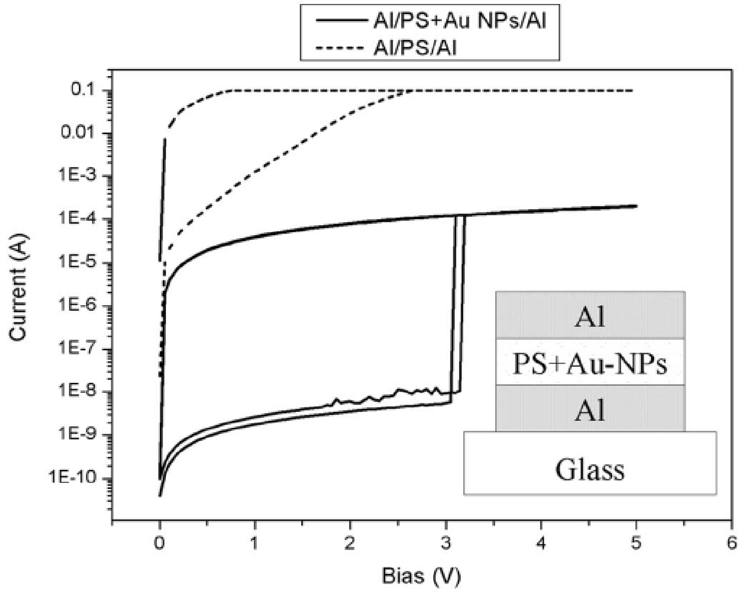


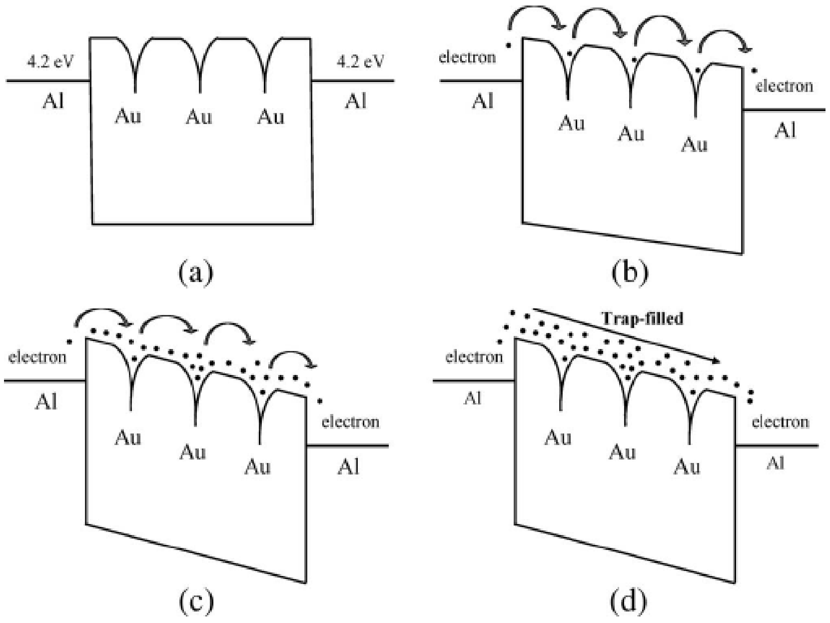
Metallic filaments from controlled insulator-metal transformation of Au nanoclusters ***[Ho et al. Nature Mater 2007 6 149]***

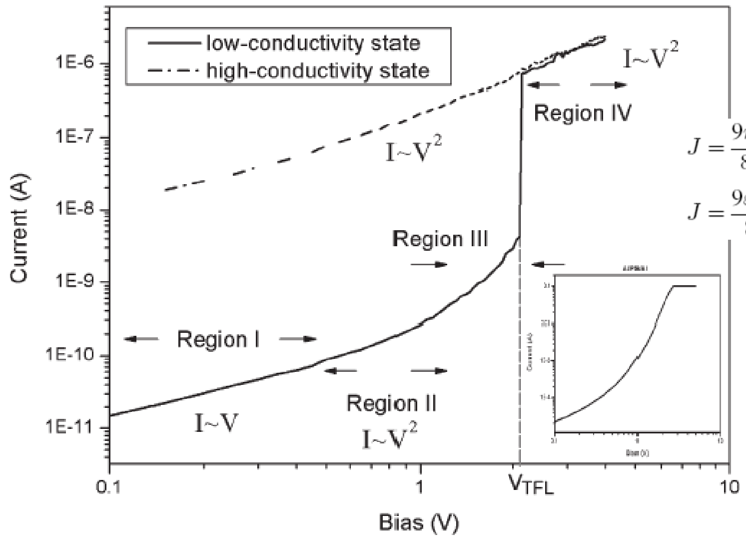


Resistive Random Access Memory (RRAM)

RRAM from Space Charges and Traps







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

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

H T Lin et al. IEEE Electron Dev Lett 2007 28 569

Resistive Random Access Memory (RRAM)

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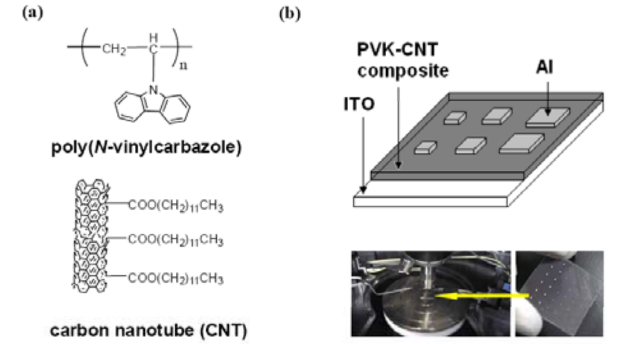
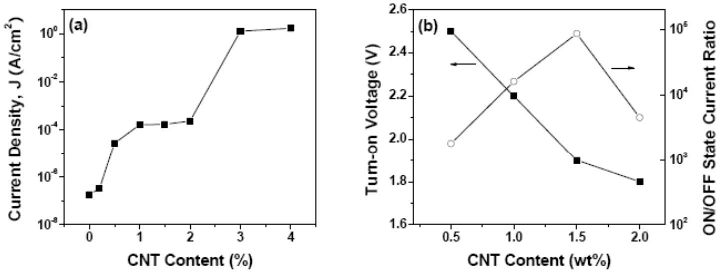
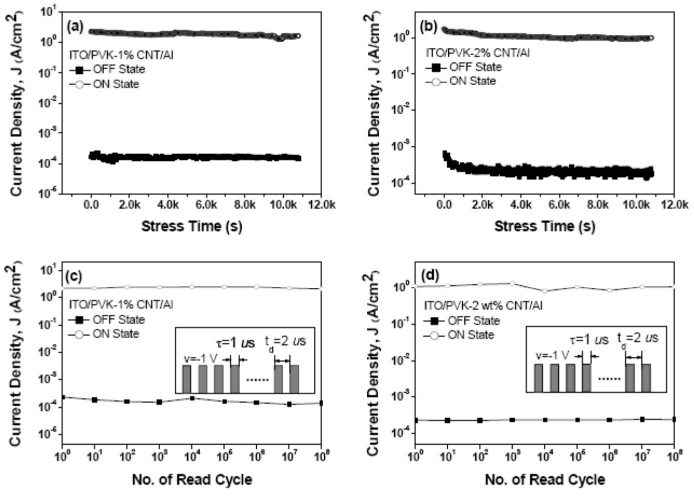
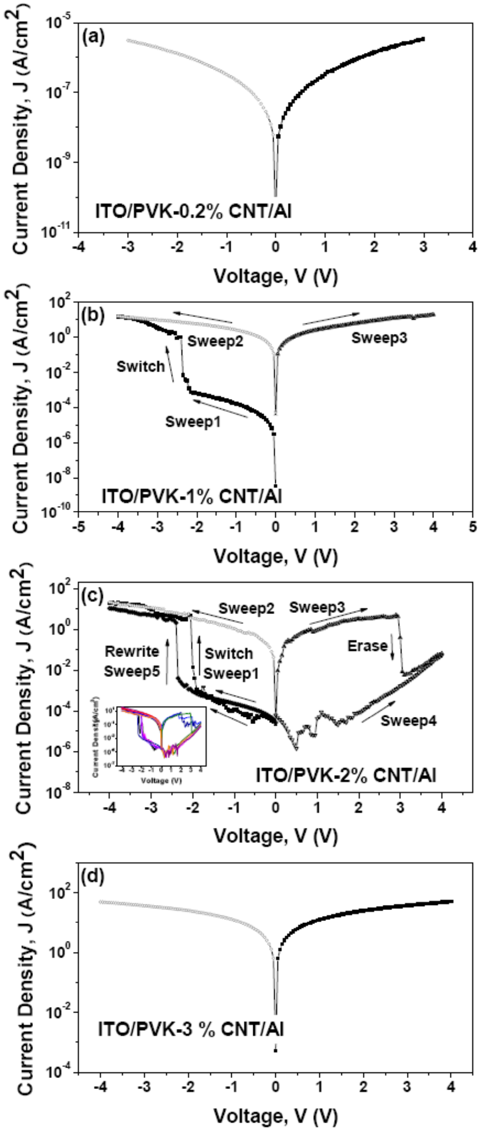
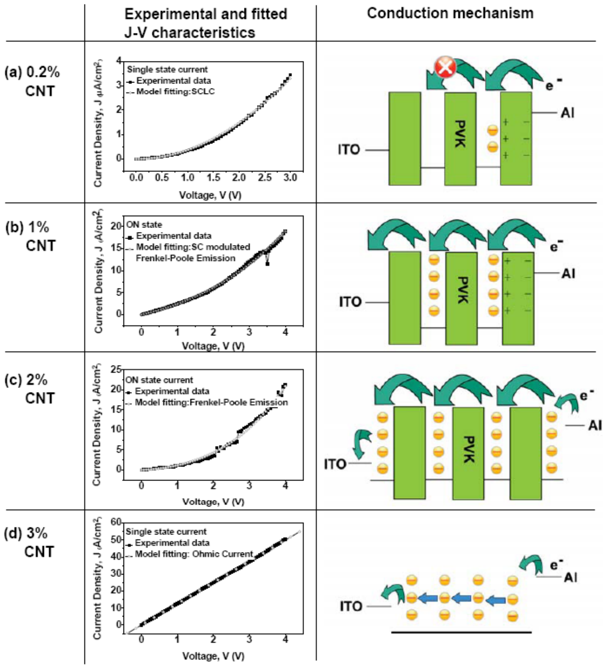
RRAM from Space Charges and Traps
Poly(*N*-vinylcarbazole)-Carbon Nanotube Composite Films











	Experimental and fitted J-V characteristics	Conduction mechanism
(a) 0.2% CNT	Single state current Experimental data Model fitting:SCLC	
(b) 1% CNT	ON state Experimental data Model fitting:SC modulated Frenkel-Poole Emission	
(c) 2% CNT	ON state current Experimental data Model fitting:Frenkel-Poole Emission	
(d) 3% CNT	Single state current Experimental data Model fitting: Ohmic Current	

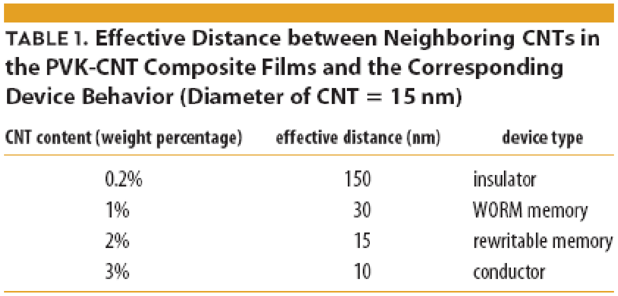


TABLE 1. Effective Distance between Neighboring CNTs in the PVK-CNT Composite Films and the Corresponding Device Behavior (Diameter of CNT = 15 nm)

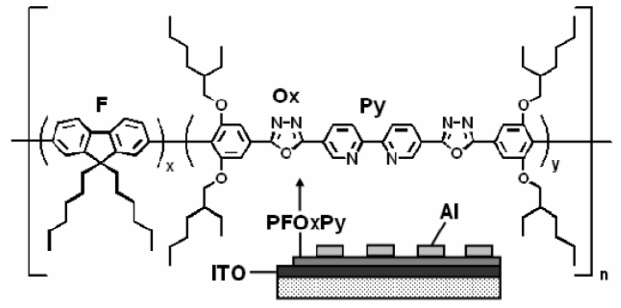
CNT content (weight percentage)	effective distance (nm)	device type
0.2%	150	insulator
1%	30	WORM memory
2%	15	rewritable memory
3%	10	conductor

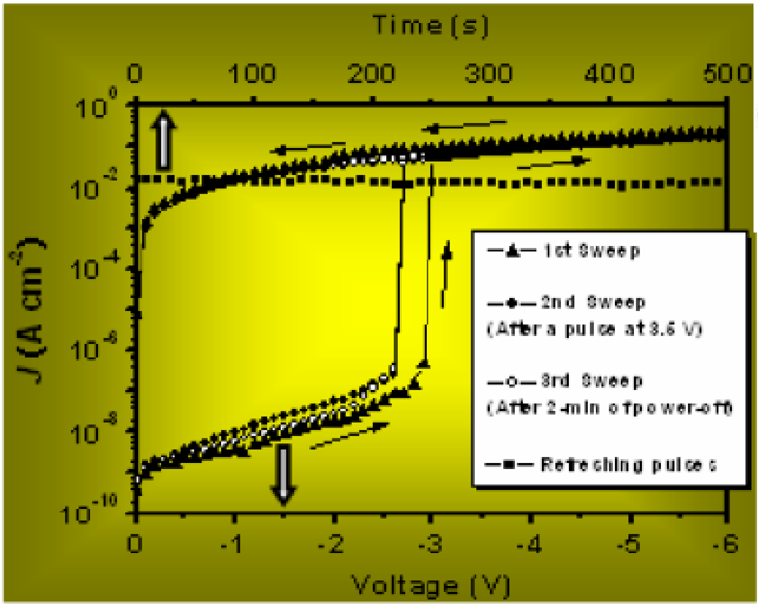
ACS NANO 2009 3 1929

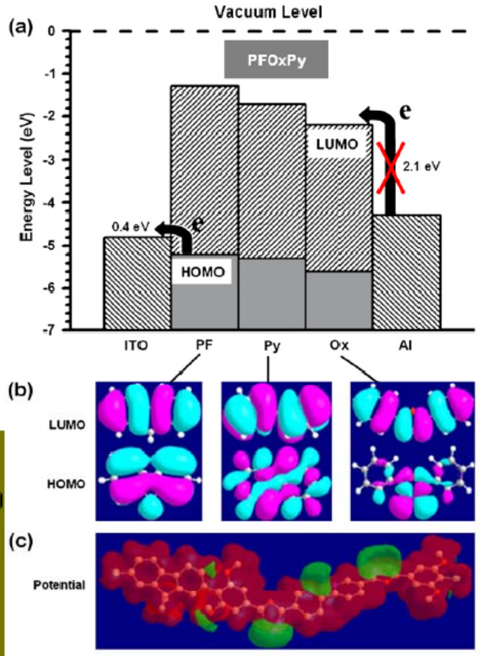
Resistive Random Access Memory (RRAM)

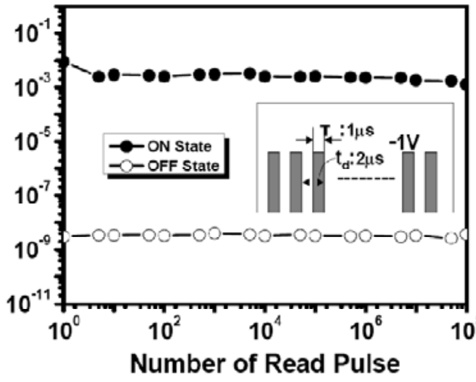
RRAM from Space Charges and Traps

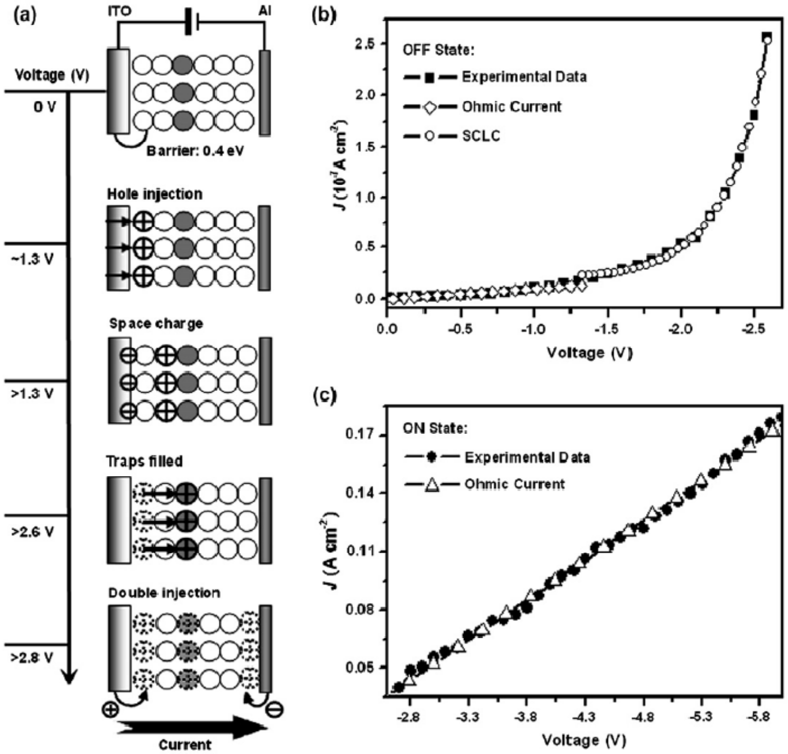
Dynamic Random Access Memory (DRAM)







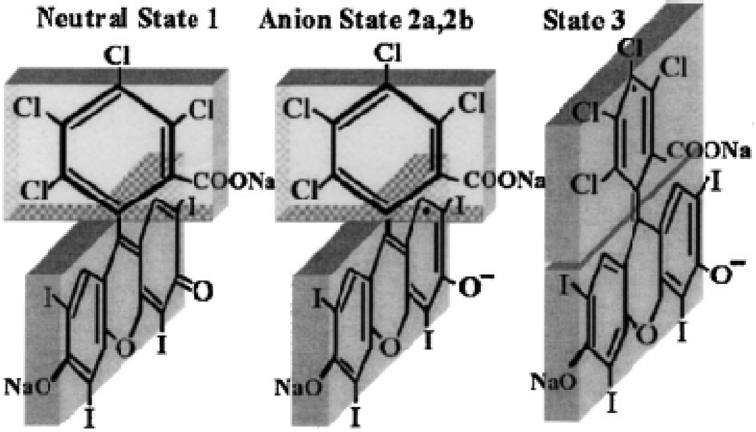


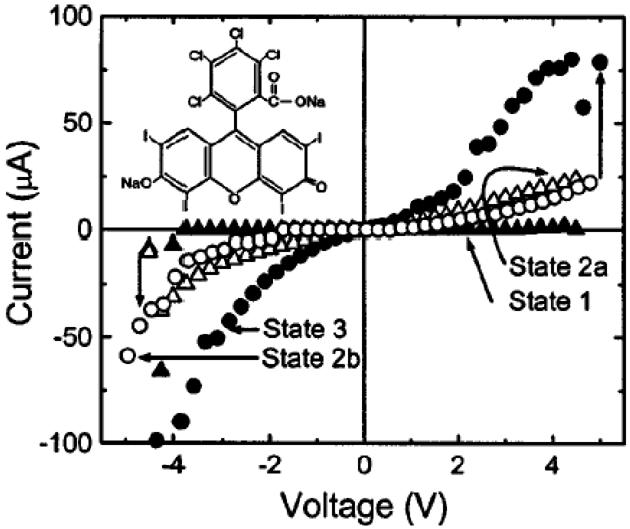


Angew Chem Int Ed 2006 45 2947

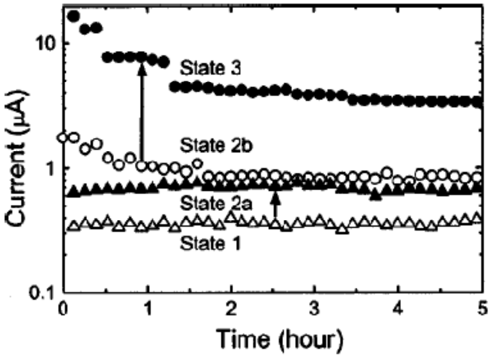
Resistive Random Access Memory (RRAM)

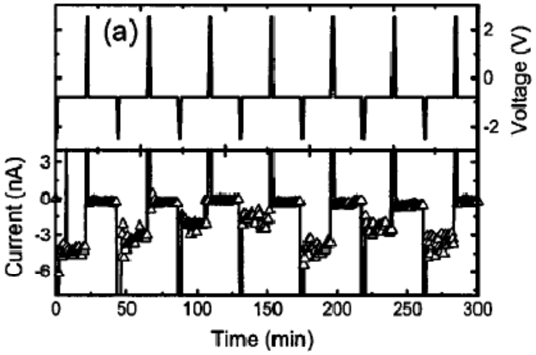
RRAM from Conformation Change Effects

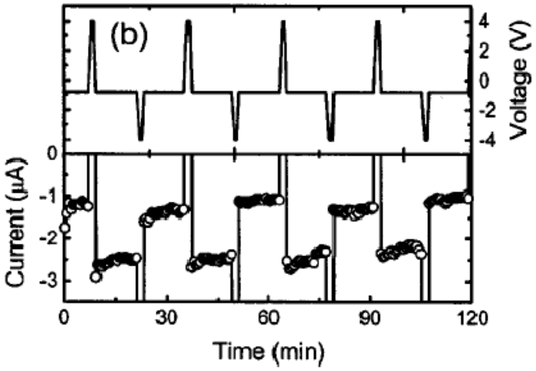




A J Pal et al. Appl Phys Lett 2004 84 999







Resistive Random Access Memory (RRAM)

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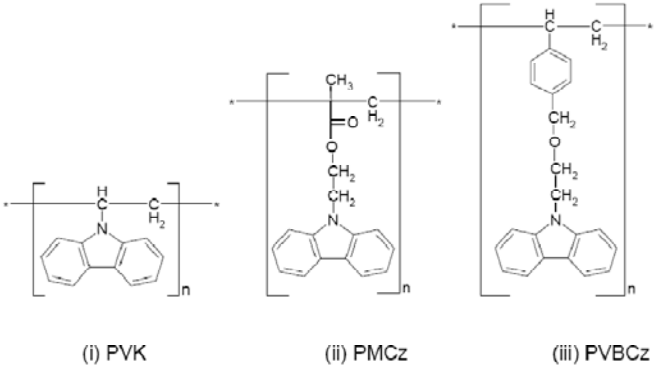
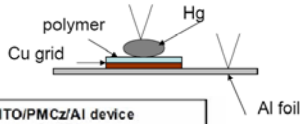
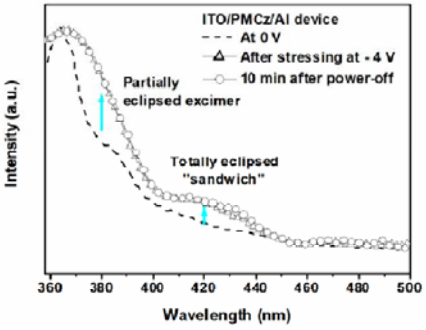
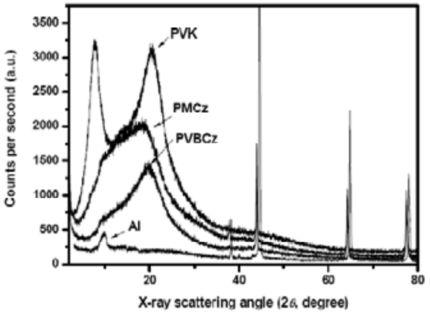
RRAM from Conformation Change Effects

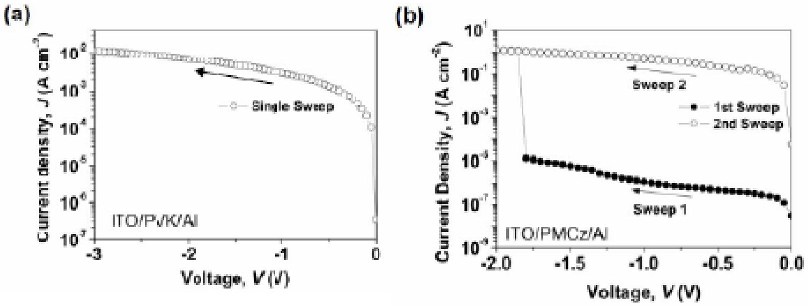


None **WORM** **Volatile**

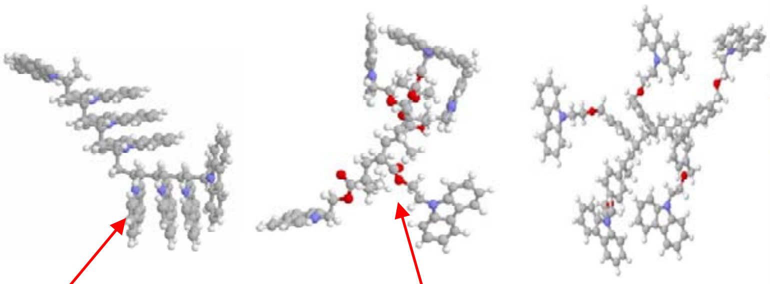


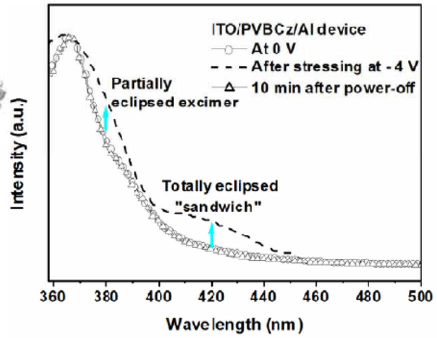


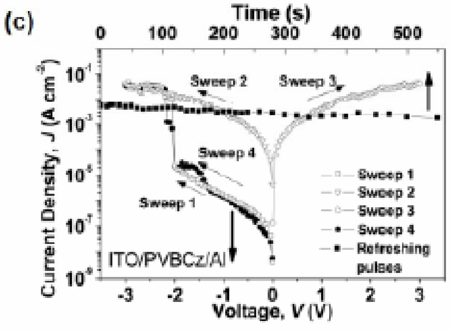


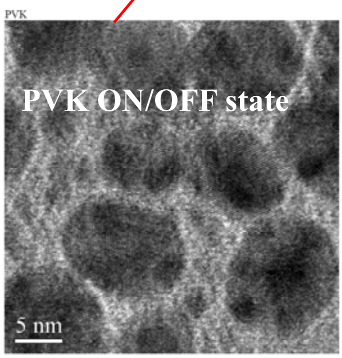


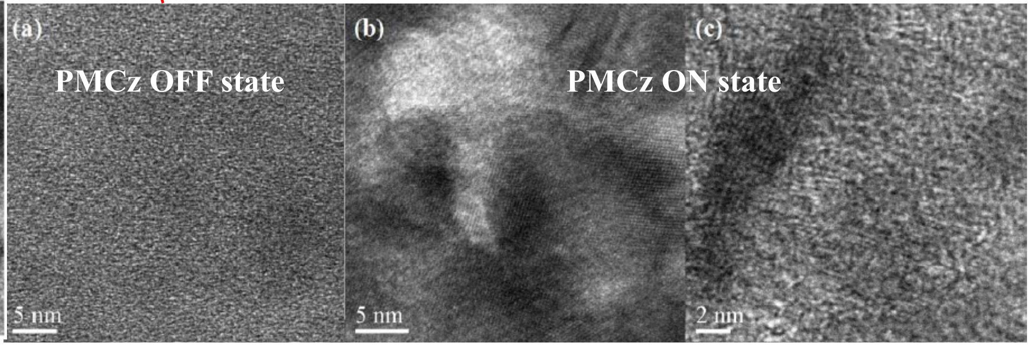
PVK **PMCz** **PVBCz**











Chem Mater 2007 19 5148

Resistive Random Access Memory (RRAM)

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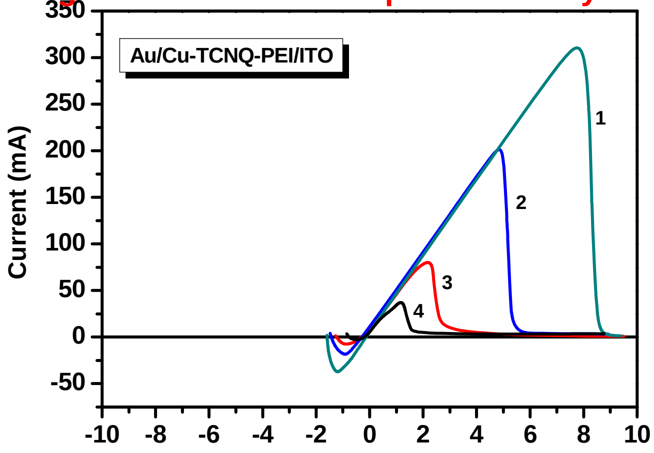
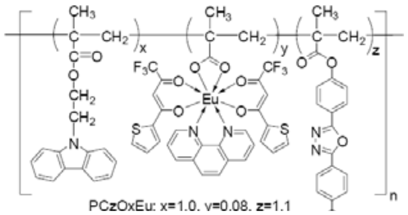
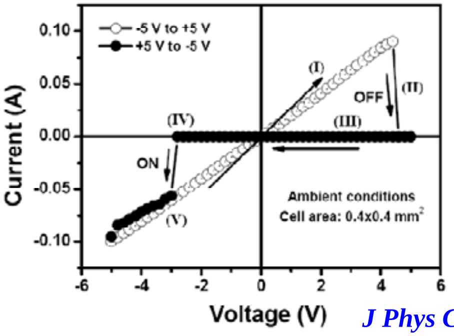
RRAM from Charge Transfer (CT) Effects

Organometallic CT Complexes in Polymers



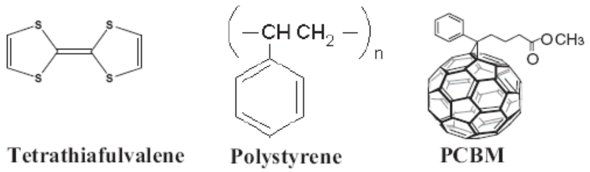
Gong & Osada, Appl Phys Lett 1992 61 2787



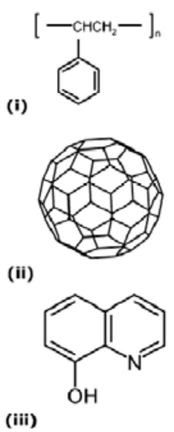


J Phys Chem B 2006 110 23995

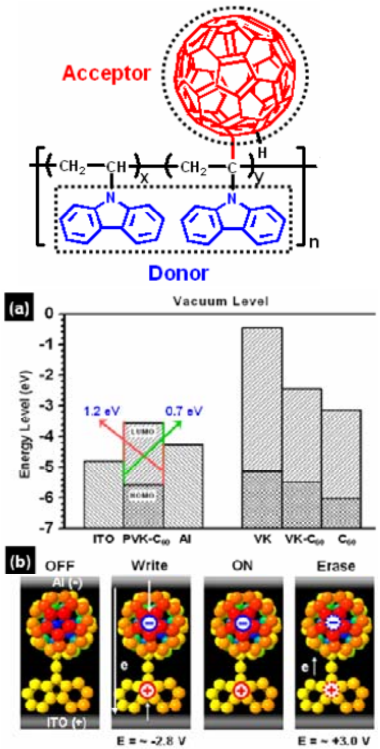
Rewritable D-A(C_{60}) Complexes



Y Yang et al. Adv Mater 2005 17 1440

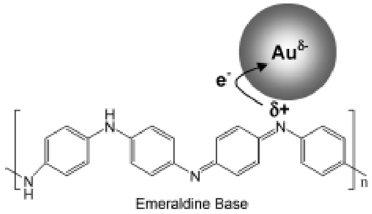


S Paul, IEEE Trans Nanotechnol 2007 6 191

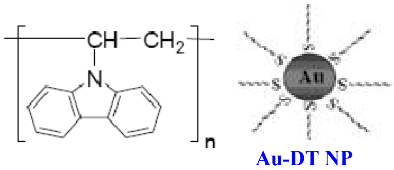


Langmuir 2007 23 312

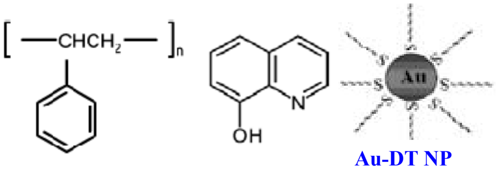
Rewritable D-A(AuNP) Complexes



Y Yang et al. Nano Lett 2005 5 1077

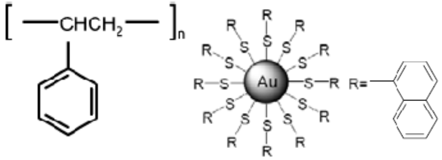


IEEE Electron Dev Lett 2007 28 107



Y Yang et al. Nature Mater 2004 3 918

WORM D-A(AuNP) Complexes

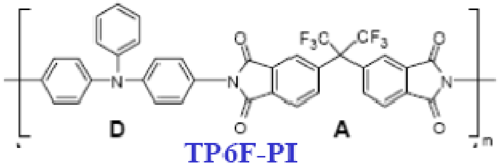


Y Yang et al. Appl Phys Lett 2005 86 123507

Resistive Random Access Memory (RRAM)

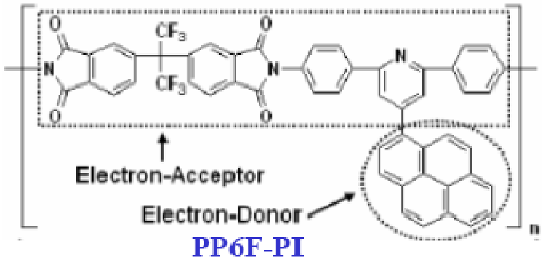
RRAM from Charge Transfer (CT) Effects

Functional Polyimides Containing Electron Donor(D) and Acceptor(A) Moieties



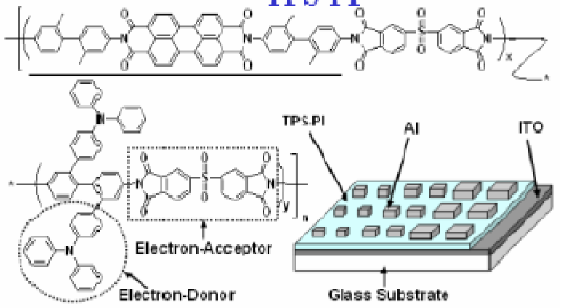
TP6F-PI

$T_g = 312°C$



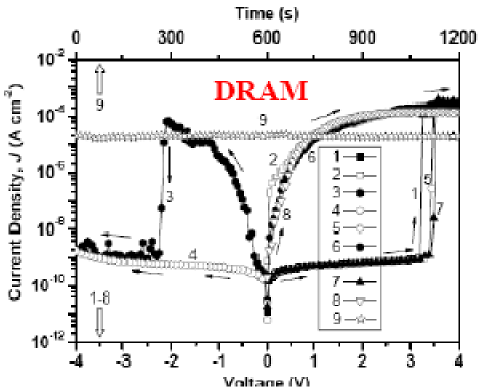
PP6F-PI

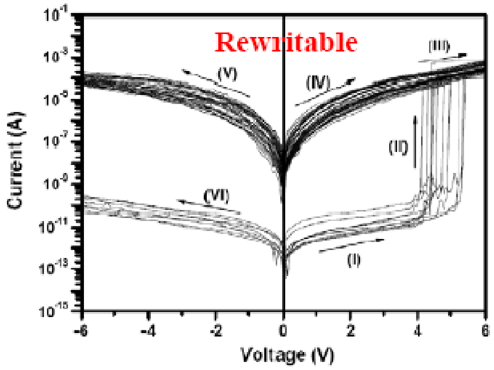
TPS-PI

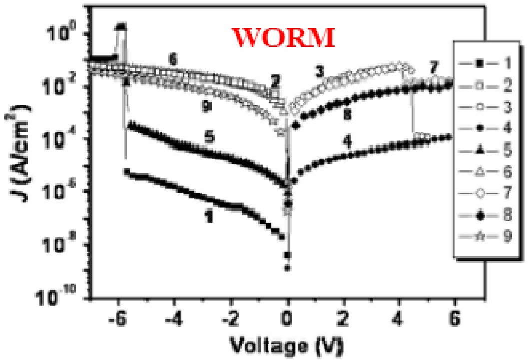


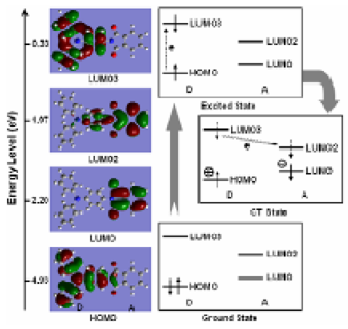
J Am Chem Soc 2006 128 8732

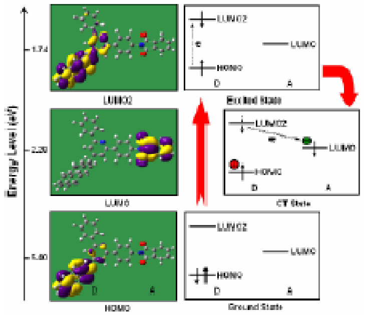
Polymer 2007 48 5182 (Feature art.)

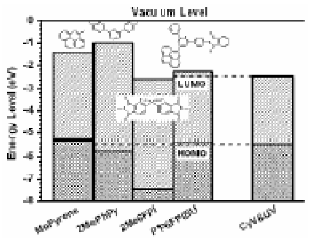


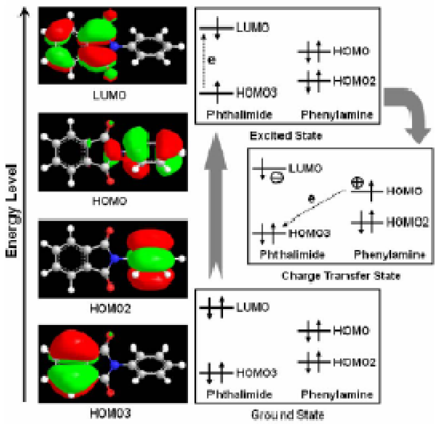








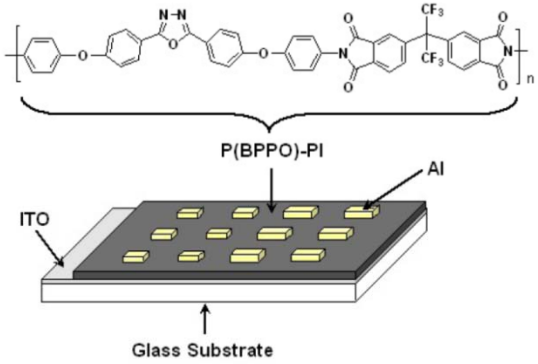


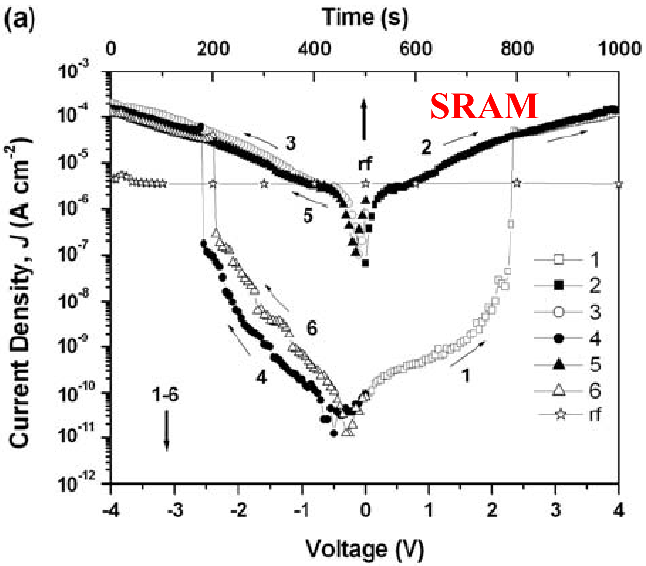


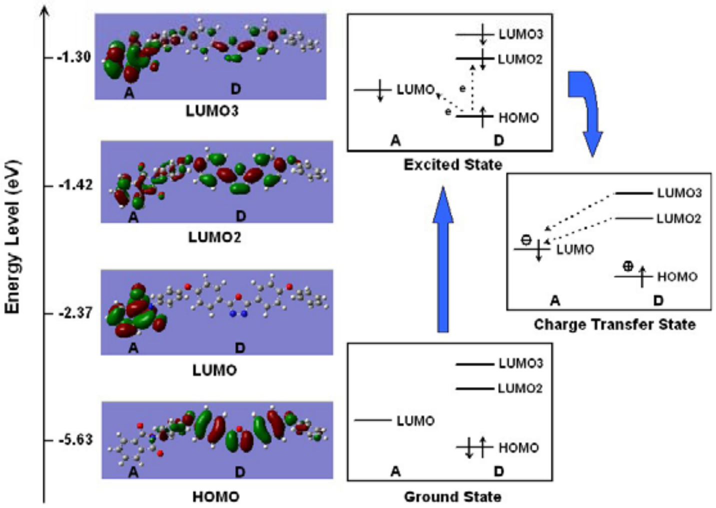
Resistive Random Access Memory (RRAM)

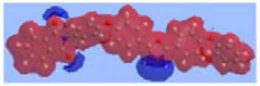
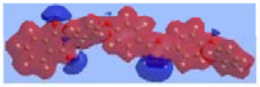
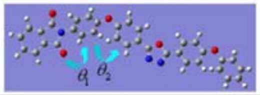
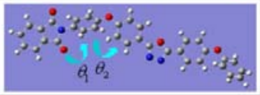
RRAM from Charge Transfer (CT) Effects
Static Random Access Memory (SRAM)

Functional Polyimides Containing Electron Donor(D) and Acceptor(A) Moieties







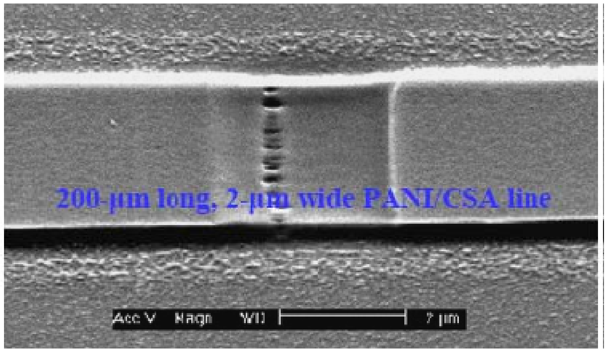
Properties	Ground State	Excited State
Dipole Moment	2.82 Debye	3.06 Debye
ESP Surface		
Optimized Geometry	 θ_1 θ_2	 θ_1 θ_2
Dihedral Angle	$\theta_1 = 40.1°$, $\theta_2 = 67.1°$	$\theta_1 = 54.6°$, $\theta_2 = 72.7°$

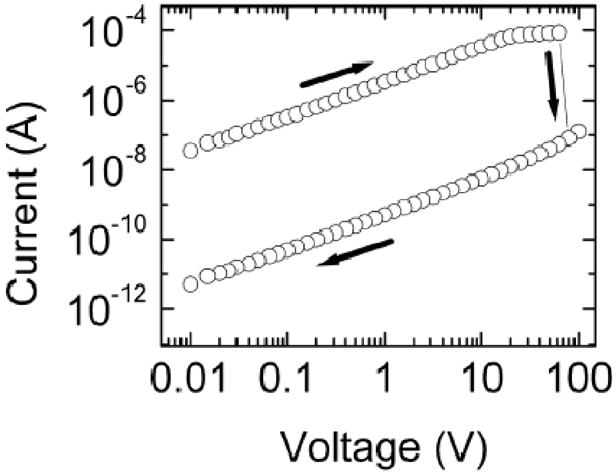
Chem Mater 2009 21 3391

Resistive Random Access Memory (RRAM)

RRAM from Polymer Fuse Effects

Doped Polyaniline Fuse-ROM

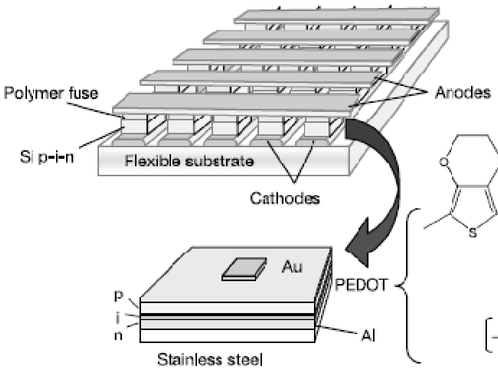


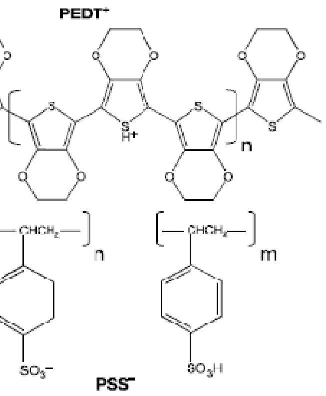


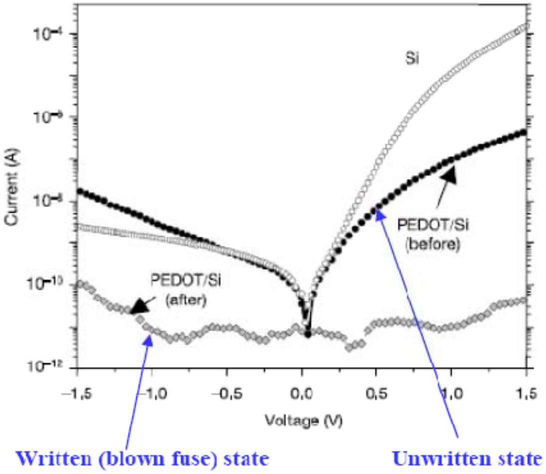
A W Marsman et al. J Mater Res 2004 19 2057

The working mechanism relies on irreversible reduction of the electrical conductivity by Joule heating like electrical safety fuses.

A Polymer/Semiconductor WORM Memory







Written (blown fuse) state

Unwritten state

S Forrest et al.
Nature 2003 426 166
Appl Phys Lett 2006 89 142109

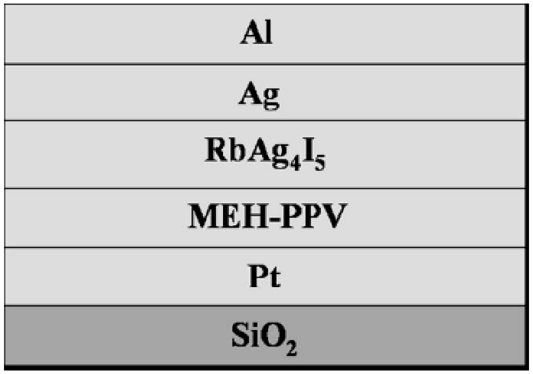
The WORM memory pixel exploits a mechanism of current-controlled, thermally activated un-doping of a two-component electrochromic conducting polymer (PEDOT)

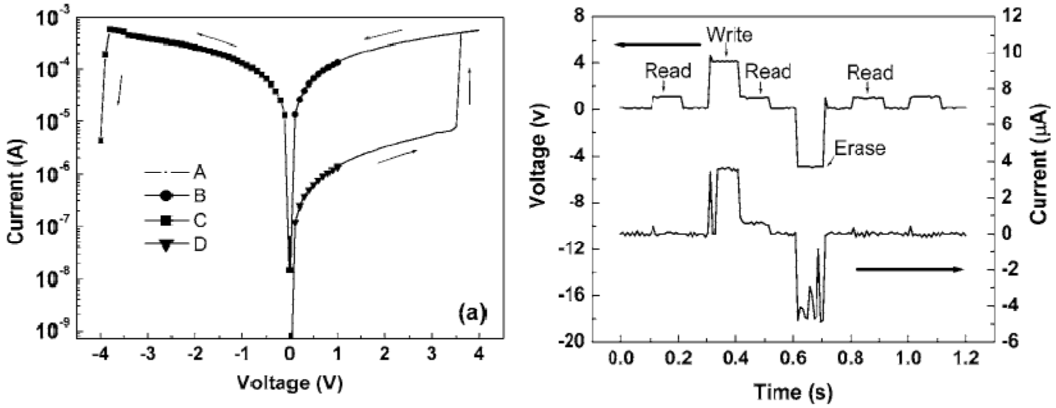
The ratio of PEDT+ to PSS- near the interface changes due to phase segregation in the presence of the applied high field, leading to a decrease in film conductivity by 6 orders

Resistive Random Access Memory (RRAM)

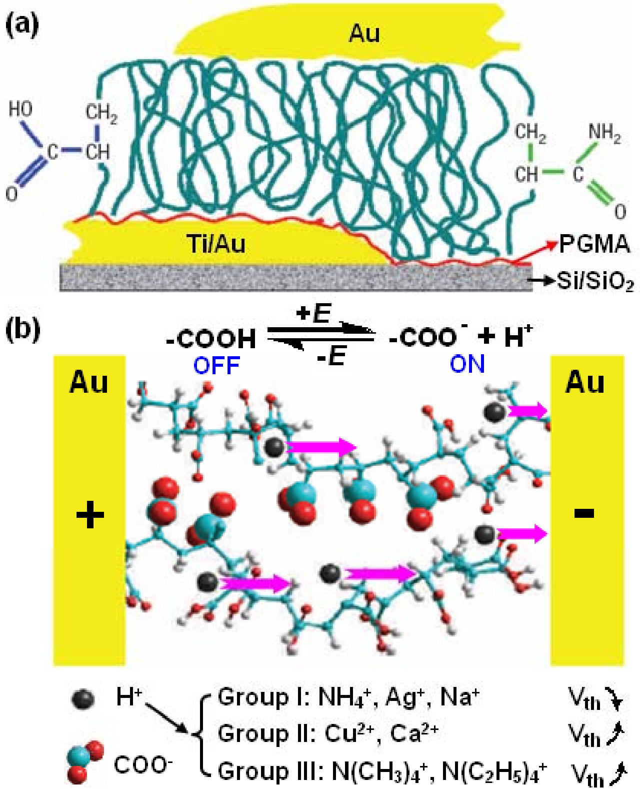
NUS
National University of Singapore

RRAM from Ionic Conductions





The conductance switching is attributed to the injection/depletion of iodide dopant ions in the MEH-PPV layer by the applied electric field



The electronic levels are created by ionization of carboxyl groups. Cations are separated but not completely removed from the system. The conductive channel is formed by a chain of COO- anions. An electric field of opposite polarity, which forces cations back, facilitates the recombination of the ionized centres in the conducting channel

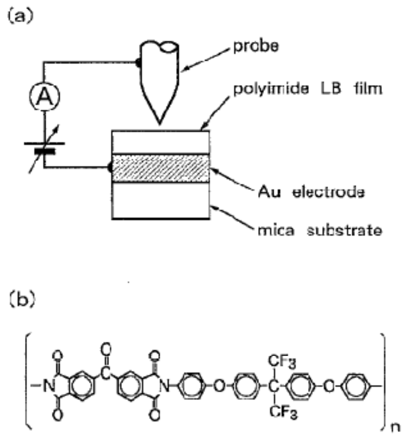
F Wudl et al. Appl Phys Lett 2006 88 133515

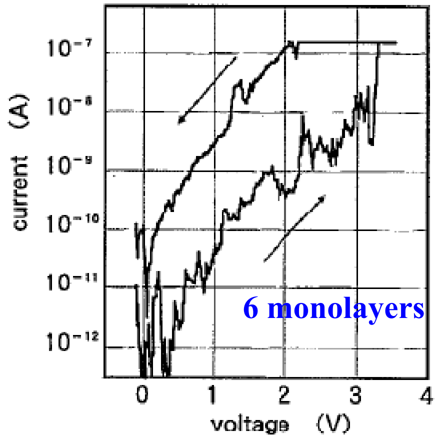
N B Zhitenev Nat Nanotechnol 2007 2 237

Resistive Random Access Memory (RRAM)

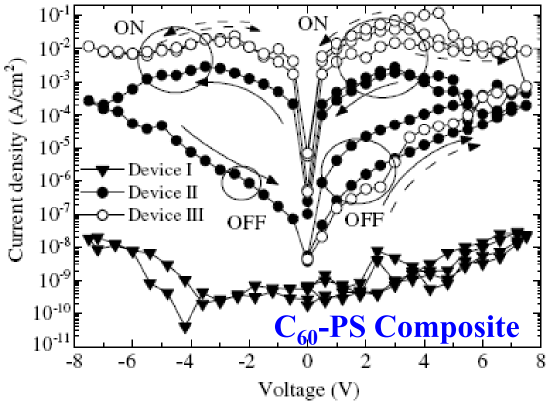
RRAM from Tunneling Effects

Memory Switching in LB Film with STM





K Takimoto Appl Phys Lett 1992 61 3032

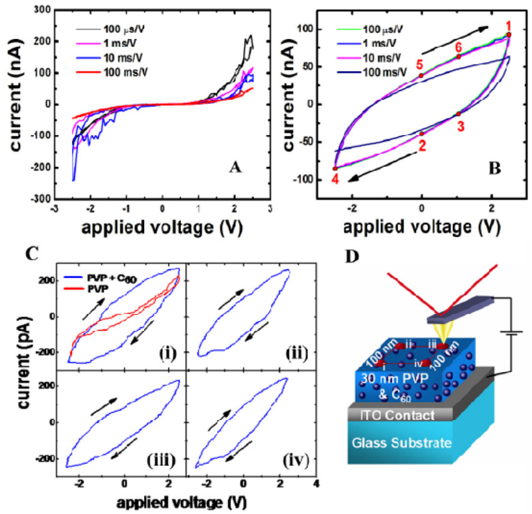


Device I: C60%(wt)=1.0-5.0%, an insulator)

Device II: C60%(wt)=5.0-7.5%, bistable switching))

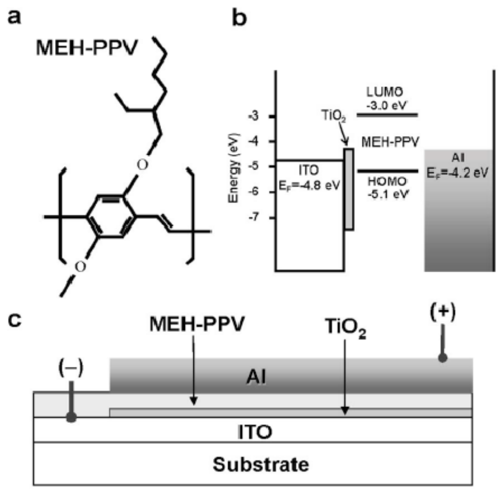
Device III: C60%(wt)=7.5-20%, WORM)

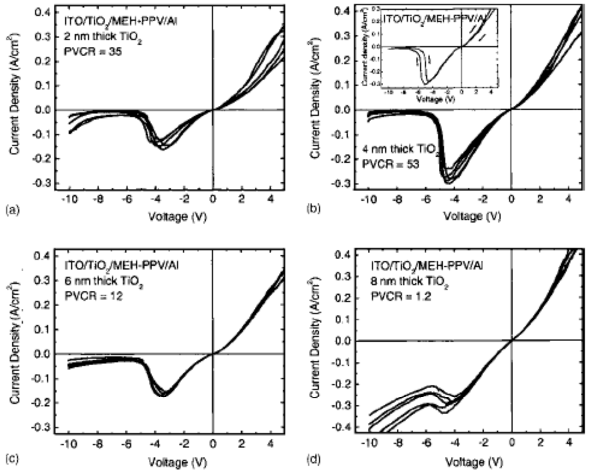
H S Majumdar et al. Org Electron 2005 6 188



S Paul Nanotechnology 2006 17 145

NDR in MEH-PPV Tunnel Diode

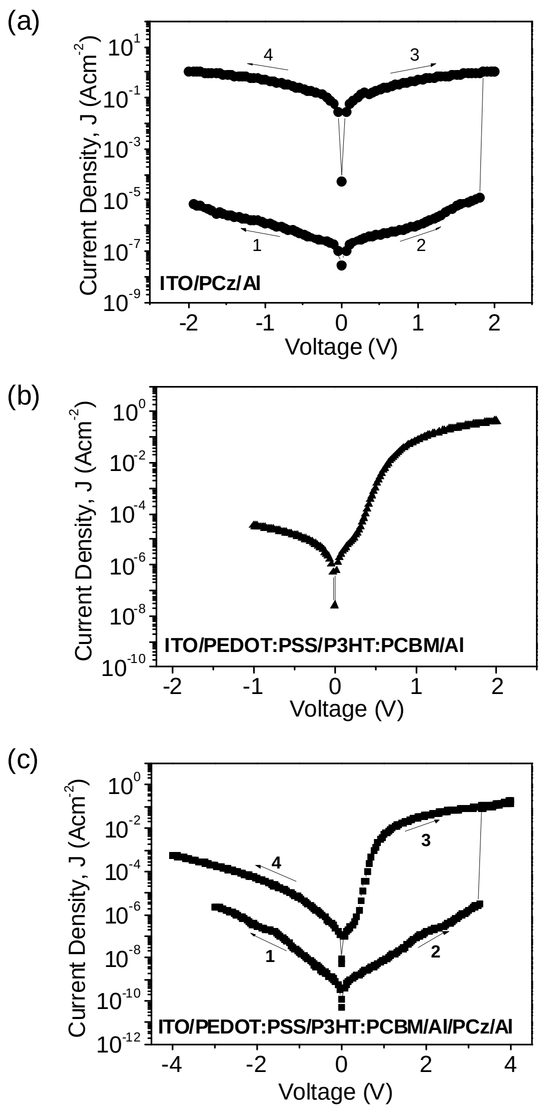


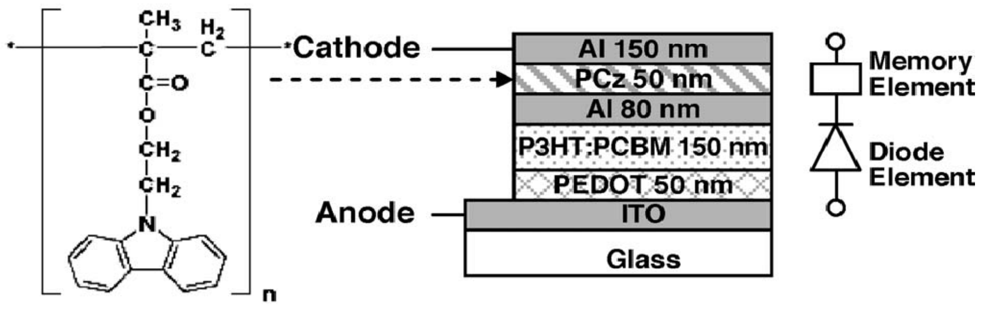


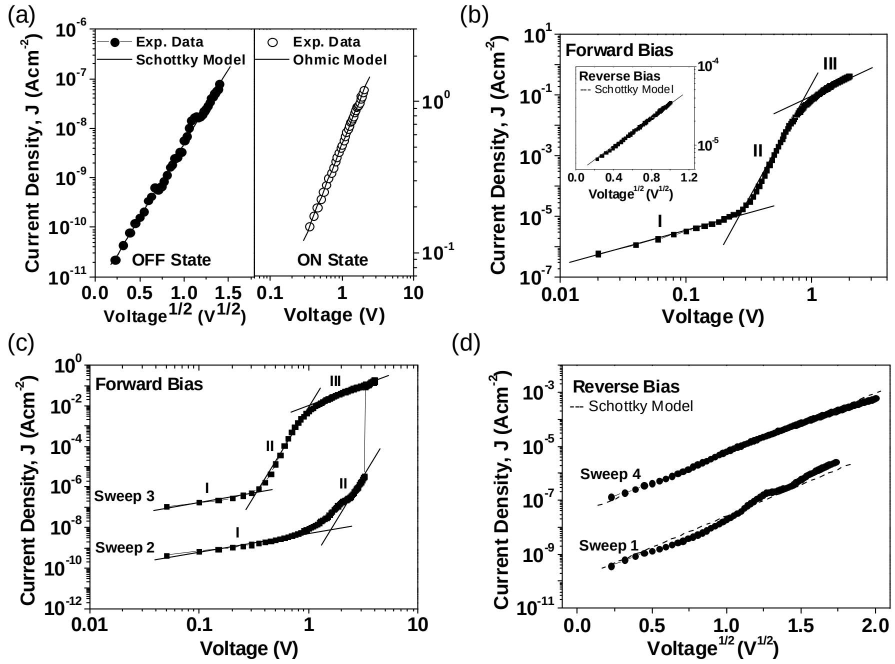
W J Yoon et al. Appl Phys Lett 2005 87 203506

Resistive Random Access Memory (RRAM)

WORM memory with rectifying property







Eric Teo, et al, IEEE EDL, Vol.30, No. 5, 2009.

Thank you!