Polymer Electronic Memories: Materials, Devices and Mechanisms

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**Polymer and Molecular Memories**

**Types of Memory**

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

**Definitions**

- **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)

A. Stikeman, Technol Rev 2002 105 31
### Classification of Polymer Memories

#### Mechanistic Analogy Between the Polymer Memory Elements and the 3 Primary Circuit Elements

<table>
<thead>
<tr>
<th>Type</th>
<th>Capacitor-type polymer memories</th>
<th>Transistor-type polymer memories</th>
<th>Resistor-type polymer memories</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical description</strong></td>
<td>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.</td>
<td>Charge storage and polarization in the dielectric layer or interfaces of an organic field effect transistor, indicating the bit level of an OFET memory.</td>
<td>Data storage is based on the high and low conductivity states (electrical bistability) of resistor in response to the applied electric field.</td>
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</table>
| **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 | Ferroelectric polymer can maintain permanent electric polarization that can be repeatedly switched between two stable states by an external electric field. | (a) Insulating polymers  
(b) Isolated chromophores, donors and acceptors  
(c) Semiconducting polymers  
(d) Composite materials |
| **Mechanism** | Polymer composition, crystallinity, film thickness, switching dynamics, film defects, metal electrodes, field pulses, fatigue characteristics | 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** | (a) Destructive read-out  
(b) Material degradation  
(c) Capacitor scaling | 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) Thickness control of dielectric layer  
(b) Parasitic capacitance  
(c) Charge coupling | (a) Mechanisms unascertained  
(b) Reproducibility  
(c) Parasitic leakage current |
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) $5 \times 5$ testing polymer devices and the basic configuration of a memory cell,
(b) a $5$ (Word line) $\times 5$ (Bit line) cross-point memory array,
(c) a $2$ (Stacked layer) $\times 5$ (Word line) $\times 5$ (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

(a) Carbon-rich filaments

Pristine → Formed → Ruptured → Reformed

(b) Metallic filaments

OFF → Write → ON → Erase

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

Resistive Random Access Memory (RRAM)

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

Resistive Random Access Memory (RRAM)

RRAM from Conformation Change Effects

None  WORM  Volatile

Chem Mater 2007 19 5148
Resistive Random Access Memory (RRAM)

RRAM from Charge Transfer (CT) Effects

Organometallic CT Complexes in Polymers

Rewritable D-A(C_{60}) Complexes

Rewritable D-A(AuNP) Complexes

Y Yang et al. Adv Mater 2005 17 1440

Gong & Osada, Appl Phys Lett 1992 61 2787

S Paul, IEEE Trans Nanotechnol 2007 6 191

J Phys Chem B 2006 110 23995

IEEE Electron Dev Lett 2007 28 107


Langmuir 2007 23 312

Resistive Random Access Memory (RRAM)

RRAM from Charge Transfer (CT) Effects

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

TP6F-PI

$T_e = 312°C$

DRAM

Rewritable

WORM

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

SRAM

Chem Mater 2009 21 3391
Resistive Random Access Memory (RRAM)

RRAM from Polymer Fuse Effects

Doped Polyaniline Fuse-ROM

200-μm long, 2-μm wide PANT/CSA line

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


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

A Polymer/Semiconductor WORM Memory

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)

**RRAM from Ionic Conductions**

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<tbody>
<tr>
<td>Al</td>
<td>Ag</td>
<td>RbAg₄I₅</td>
<td>MEH-PPV</td>
</tr>
<tr>
<td>Pt</td>
<td>SiO₂</td>
<td></td>
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</table>

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.

Resistive Random Access Memory (RRAM)

RRAM from Tunneling Effects

Memory Switching in LB Film with STM

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

NDR in MEH-PPV Tunnel Diode

C60-PS Composite


S Paul Nanotechnology 2006 17 145

K Takimoto Appl Phys Lett 1992 61 3032
Resistive Random Access Memory (RRAM)

WORM memory with rectifying property

Thank you!