Redox-Active Molecular Flash Memory for On-Chip Memory

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Outline

- Introduction
- Molecule attachment method & characterizations
- Molecular charge-trapping memory
  - Ferrocene molecule for fast and reliable NVM
  - (Ru)₂ molecule for multi-bit NVM
- Molecular Flash memory
  - Self-aligned SiNW FETs
  - Integration of redox molecules in Flash memory
- Summary
Introduction: non-volatile memory

On-chip memory in central process unit (CPU)
- Dynamic random access memory (DRAM)
- Static RAM (SRAM) – cache memory

- Occupy large floor space
- Consume high operation power
- Volatile

Non-volatile memory as the on-chip memory in CPUs
Non-volatile memory

- **Non-volatile memory (NVM)**
  - Speed
  - Reliability
  - Integration density
  - Manufacture cost

Not suitable for use as primary storage or on-chip memory

- **Next generation NVM**
  - Flash memory
  - Ferroelectric RAM
  - Phase-change RAM
  - Resistive RAM
  - Magnetoresistive RAM
Flash memory

- **Floating-Gate NVM**
  - Control Gate
  - Inter Ploy Dielectric
  - Floating Gate
  - Tunnel Oxide
  - p-Si substrate

- **Charge-trapping NVM**
  - Simple structure
  - Better scalability
  - Low power
  - Less sensitivity to the SILC

Charge Trapping NVM

- Silicon-oxide-nitride-oxide-silicon (SONOS)
- Nitride-base read-only memory (NROM)
- Nanocrystal memory (NCM)
SONOS charge-trapping NVM

- Thinner tunnel oxide for faster P/E speed
  - poor retention and stability
- Thicker blocking oxide to suppress leakage current
  - larger operation voltage

**SONOS-like NVM**

**Novel charge-trapping mediums:**
- New high-k materials
- Organic semiconductor
- Redox-active molecules
Introduction: molecular NVM

- Redox-active molecules as charge trapping medium
  - Better reliability – endure more than $10^{12}$ P/E cycles
  - Intrinsic redox centers provides naturally distinct charged states
  - Lower operation voltage
  - Higher speed
  - Higher integration density
  - Simple and low-cost process

- Redox molecules in solid-state flash memory
  - CMOS compatible
  - Embedded molecules for better stability
  - Regular electronics characterization metrologies
Strategies to enhance memory density

- More devices per unit of volume by using 3D integration (complicated and high-cost process);
- Embedded nanocrystal (controlling of size and density)
- Multiple dielectric charge storage layers (stack engineering and cell size)
- Redox-active molecules with multiple redox centers
Self-assembled monolayer (SAM) on H-Si or SiO\textsubscript{2} surfaces

- Simple and low-cost attaching process:
  - Solution of molecules in dichloromethane;
  - Wafer soaking or dropping droplets of solution;
  - \(\sim 100\) °C in inert environment.
- Different molecules with different linker
Molecule attachment characterizations

- Surface coverage of $5.23 \times 10^{13}$ cm$^{-2}$ and $3.14 \times 10^{13}$ cm$^{-2}$ for SAM on Si and SiO$_2$

- SAM survives the deposition of ALD Al$_2$O$_3$
Molecular charge-trapping NVM

\[ \Delta V_{FB} = \frac{q \cdot n}{C} = q \cdot n \left( \frac{T_{Al_2O_3}}{\varepsilon_0 \varepsilon_{Al_2O_3}} + \frac{T_{linker}}{\varepsilon_0 \varepsilon_{linker}} \right) \]

Charging density was calculated as \(4.41 \times 10^{12} \text{ cm}^{-2}\)
Intrinsic redox behavior of the Ferrocene molecule

- Good gate stack interfaces

**Excellent endurance:**

- Program ΔV_{FB} [V]
- Erase ΔV_{FB} [V]

**MAFOS vs. MAFS**

- Good retention compared with MAFS

**Number of P/E Cycles**

- MAFOS
- MAFS

- Program: 10 V, 500 μs
- Erase: -10 V, 500 μs

**ΔV_{FB} [V]**

- -0.6 to 0.6

- 10^0 to 10^10

**Number of P/E Cycles**

- 10^0 to 10^10

**ΔV_{FB} [V]**

- -0.6 to 0.6

- 10^0 to 10^10
Molecules with multiple redox states

- Work in progress:
  - Attachment characterization: XPS, CyV, FTIR;
  - Planar memory devices.
Si Nanowire FET Platform

- Self-aligned gate-surrounding SiNW FET

Patterned Au catalyst

Si Nanowire

Source/Drain

Gate

Al₂O₃

Top Gate

Si NW

Source

Drain

40 nm Al gate

Al₂O₃

HfO₂

SiNW

SiO₂
- High ON/OFF current ratio
- Small subthreshold slope
- Small leakage current
Molecular Flash based on SiNW FET

- Large memory window
- High On/Off ratio
- Negligible memory window in reference sample (without molecule layer)

Redox-active ferrocene attaching on SiO₂ tunneling layer
Molecular flash based on SiNW FET

- Fast P/E speed
- Effective charge separation by SiO₂ tunneling barrier
Molecular NVM based on SiNW FET

- Better data retention due to optimized tunneling SiO₂
- Behave well after $10^9$ P/E cycles
Summary

- Redox-active molecules were implemented for advanced flash memory devices with excellent endurance ($10^9$ P/E cycles), and are very attractive for future on-chip memory applications;
- Selective molecules with simple structure and multiple redox states for Flash memory with better performance;
- Multi-bit storage in molecular Flash memory can be realized by employing multiple redox states molecules.
Thank you!