High-Performance Molecular FLASH Memory with Redox-Active Molecules

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The dimensional scaling of microelectronics to improve the performance of the central process unit (CPU) is facing fundamental and physical challenges. The current solution is to increase the cache memory – static random access memory (SRAM). [1] However, this will decrease CPU information throughput because SRAM is volatile and occupies a large floor space. Therefore, developing high-performance non-volatile memory as local memory in CPU will bring a revolutionary impact to microelectronics which increasingly demands stand-alone and embedded memory for portable electronics. [1] Floating-gate non-volatile memory (NVM) is compatible with CMOS integration. However, the traditional floating gate materials, such as poly-Si/SiO_2 and oxynitride, require large Program/Erase (P/E) voltage and endure only 10^6 P/E cycles [2]. Therefore the conventional floating-gate NVM cannot be used for local memory.

Redox-active molecules have been recently considered as attractive floating gate materials for charge storage. [3] It has been demonstrated that the redox-active molecules attached on Si structures were stable in harsh conditions and endured more than 10^{12} P/E cycles. [4] These excellent performances are naturally derived from the intrinsic properties of redox molecules. Redox molecules usually have one or multiple redox states and can be engineered to attach on various surfaces forming self-assembled monolayer (SAM) or multi-layers with simple and low-cost processes. Typically, applying an oxidation voltage will cause electron loss in redox molecules; reversely, under a reduction voltage, electrons will be driven back to the molecules. Due to the inherent oxidation and reduction of the redox centers, molecules can exhibit distinct charged or discharged states, which can be deemed as logic on and off states, with very fast write/erase speed and excellent endurance. These properties make redox molecules very promising candidates for applications in charge-storage non-volatile memory devices, such as FLASH memory and dynamic random access memory (DRAM). Moreover, due to the scalability of molecules and the naturally-derived multiple redox states for robust charge storage, the molecular memory density can be much higher than the conventional memory devices.

The integration of redox-active molecules into a solid-state structure is preferred for the consideration of compatibility with CMOS fabrication process. [5] But the device Programming/Erasing (P/E) endurance and speed have not yet been well studied. In this work, we fabricated and measured non-volatile memory capacitors based on metal-Al_2O_3-ferrocene-SiO_2-silicon (MAFOS) hybrid structure which contains Ferrocene SAM on SiO_2. As shown in Figure 1 – Figure 4, we have studied the Si-molecular integration and the charge storage properties the MAFOS capacitors and FLASH memory cells. The devices exhibited high P/E speed and excellent endurance: the device remained functional after 10^9 P/E cycles. This work shows that the hybrid integration of redox-active molecules with semiconductor platform is attractive for high-performance NVM applications.

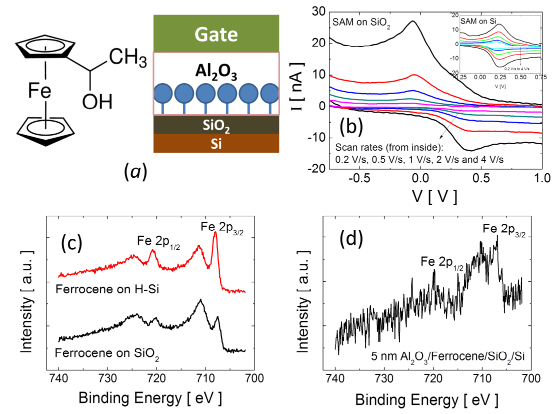

Fig. 1 (a) Ferrocene molecular structure and schematic of gate stack; (b) cyclic voltammetry of electrolyte-ferrocene-SiO_2-Si capacitor; (c) and (d) XPS of Ferrocene on Si and SiO_2 before and after deposition of Al_2O_3 covering Ferrocene. These results indicated the Ferrocene molecules are functional after atomic layer deposition of Al_2O_3.

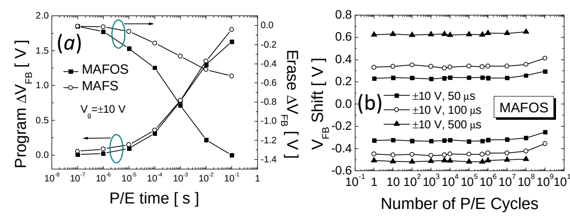

Fig. 2 Characterization of the P/E speed: (a) and endurance (b) of metal/Al_2O_3/Ferrocene/SiO_2/Si (MAFOS) and metal/Al_2O_3/Ferrocene/Si (MAFS) capacitors.

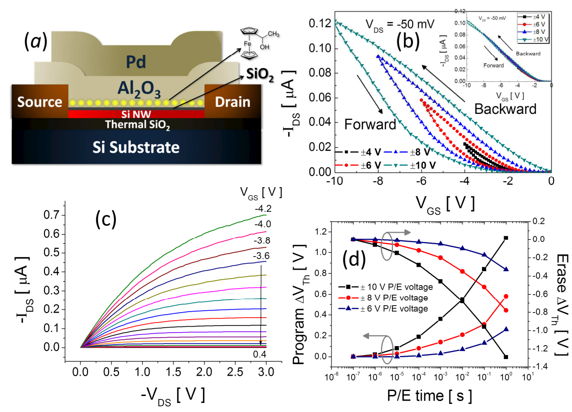

Fig. 3 (a) Schematic showing the molecular FLASH memory consisting of Si nanowire field effect transistor and MAFOS top-gate stack. (b) The charge storage in the embedded Ferrocene induced large memory window. (c) The molecular FLASH cells exhibited excellent transistor I-V characteristics. (d) Excellent P/E speed.

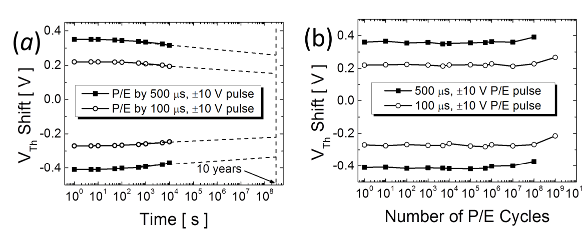

Fig. 4 The FLASH cells exhibit (a) excellent retention and (b) P/E endurance (> 10^9 cycles).

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