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# Redox-Active Molecular Nanowire Flash Memory for High-Endurance and High-Density Nonvolatile Memory Applications

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### Supporting Information

**ABSTRACT:** In this work, high-performance top-gated nanowire molecular flash memory has been fabricated with redox-active molecules. Different molecules with one and two redox centers have been tested. The flash memory has clean solid/molecule and dielectric interfaces, due to the pristine molecular self-assembly and the nanowire device self-alignment fabrication process. The memory cells exhibit discrete charged states at small gate voltages. Such multibit memory in one cell is favorable for high-density storage. These memory devices exhibit fast speed, low power, long memory retention, and exceptionally good endurance (>10<sup>9</sup> cycles). The excellent characteristics are derived from the intrinsic charge-storage properties of the protected redox-active molecules. Such multi-bit molecular flash memory is very attractive for high-endurance and high-density on-chip memory applications in future portable electronics.



KEYWORDS: redox-active molecules, Si nanowire FETs, flash memory, endurance, multi-bit memory

## INTRODUCTION

The continuous complementary metal-oxide-semiconductor (CMOS) scaling to achieve more powerful central processing unit (CPU) is reaching the fundamental limits imposed by heat dissipation and power consumption.<sup>1</sup> This will finally stop the increase of integration density of transistors in the logic circuit of CPU which was predicted by Moore's Law. In order to increase the capability of CPU, there have been extensive efforts to develop high-performance nonvolatile memory as local CPU memory, replacing the conventional on-chip static random access memory (SRAM), which is volatile and usually occupies a large floor space.<sup>2</sup> Redox-active molecules, among all the new emerging candidates, have been considered a promising chargestorage medium in flash memory.<sup>3-7</sup> It has been demonstrated that the redox-active molecules attached onto Si structures are stable and can endure more than 10<sup>12</sup> programming/erasing (P/E) cycles.<sup>8</sup> Redox molecules have been integrated in electronic devices by forming a self-assembled monolayer (SAM) or multilayer on various Si-based surfaces with very simple and low-cost methods.<sup>9-13</sup> Such molecular electronic devices can be integrated and operated at the molecular scale,

and therefore, have potential for low-power and ultrahigh-density nonvolatile memory applications.

Integrating redox-active molecules with the semiconductor field-effect transistor (FET) for solid-state molecular flash memory will enhance the memory performance by utilizing the advantageous properties of redox-active molecules, and also provides an efficient platform to study the redox-active molecules with microelectronics characterization metrologies when compared with solution-based electrochemical characterization. The charge-storage behavior and memory applications of redox-active molecules have been previously studied, however, up to now, there has been no report on high-performance metal-oxide-semiconductor field-effect transistor (MOSFET)-like flash memory based on redox-active molecules.<sup>12–16</sup> MOSFETs are the fundamental elements in CMOS technology. Semiconductor nanowire and nanotube MOSFETs have been regarded as the building block for nanoelectronic devices and circuits.<sup>17–19</sup> Compared to planar devices based on

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bulk materials, the nanowires have a smaller channel and large surface-to-volume ratio. Thus, nanowire structures have the advantage of more efficient memory with less stored charge inducing a comparable memory window. Li et al. reported studies of flash memory based on a back-gate semiconductor nanowire FET structure incorporating a redox-active bis-(terpyridine)-Fe(II) molecule attached to the nanowire channel.<sup>6,20</sup> The memory devices had well-characterized molecular structure-dependent memory behavior and multibit storage, but the study did not demonstrate operation speed. While promising, these early molecule-based reports had suboptimal performance largely due to the back gate device structure, unclean steps in the FET device fabrication process, and most importantly, the absence of protection for redoxactive molecules. Moreover, the demonstrated multi-bit storage depends solely on the gate voltage applied to oxidize/reduce a portion of molecules in the SAM, which will inevitably become blurred with further cell scaling and increasing memory levels. In 2014, Busche et al. reported a study on molecular nanowire flash memory using core-shell polyoxometalate molecules for charge storage.<sup>21</sup> The memory device showed excellent properties such as good retention, high On/Off ratio, and potential multi-bit memory, but the endurance properties were not studied, which is a key characteristic for flash memory. Furthermore, the top-down nanowire preparation and device fabrication methods limited further exploration of the redox behavior and memory performance of the molecules, despite the molecules themselves being quite promising. In this work, we report a CMOS-compatible molecular nonvolatile flash memory based on self-aligned top-gate Si nanowire FET. Two different kinds of redox-active molecules have been selfassembled onto Si nanowires by using a simple and low-cost process. The molecules are effectively encapsulated by an engineered oxide dielectric, creating a structure with clean solid/molecule and dielectric interfaces. The memory behavior was systematically studied on both sets of molecular devices. These molecular flash memory cell exhibited fast P/E speed and excellent endurance with discrete charge-storage. Multi-bit storage in a one memory cell has been achieved owing to the multiple redox states in the molecule. Such excellent performance and unique properties are very promising for future applications in on-chip nonvolatile memory to replace SRAM and dynamic random access memory (DRAM).

#### RESULTS AND DISCUSSION

The molecular flash memory cells were prepared by following a self-alignment method shown in Figure 1, in a similar procedure as our previous work.<sup>22,23</sup> The redox-active molecules used in this work are  $\alpha$ -ferrocenylethanol (referred as ferrocene) and Ru<sub>2</sub>(*ap*)<sub>4</sub>(C<sub>2</sub>C<sub>6</sub>H<sub>4</sub>P(O)(OH)<sub>2</sub>) (referred as Ru<sub>2</sub>), in which *ap* = 2-anilinopyridinate, with the molecular structures shown in Figure 2.<sup>24</sup> Figure 3 shows the transmission electron microscopy (TEM) image of the cross-section of a typical molecular flash memory cell (with ferrocene molecules attached on Si nanowire channel). A clear gate-surrounding structure has been obtained. As shown in Figure 3, an "intermixed" region with a thickness of ~6 nm was observed (indicated by the red dash line). The high-resolution transmission electron microscopy (HRTEM) image in the inset of Figure 3 clearly shows the cross-section of the nanowire channel and the surrounding SiO<sub>2</sub> layer.

Unlike the liquid electrolyte-involved nonvolatile memory, our solid-state molecular flash memory has the storage



**Figure 1.** Self-aligned Si nanowire FET fabrication process: (a) patterned Au on SiO<sub>2</sub>, synthesis of Si nanowire from Au catalyst, and nanowire oxidation; (b) formation of source/drain contacts and SAM attachment; (c) deposition of  $Al_2O_3$  and formation of top gate; (d) schematic structure of a completed molecular flash memory device.



**Figure 2.** Structure of redox-active molecules (a)  $\alpha$ -ferrocenylethanol and (b) Ru<sub>2</sub>(*ap*)<sub>4</sub>(C<sub>2</sub>C<sub>6</sub>H<sub>4</sub>P(O) (OH)<sub>2</sub>).

medium-redox-active molecules attached onto the nanowire surface, encapsulated and protected with a high-quality dielectric by atomic layer deposition (ALD). Our previous work has characterized the attachment of ferrocene on SiO<sub>2</sub> surface with X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV) measurements, showing that the ferrocene coverage density was  $3.14 \times 10^{13}$  cm<sup>-2</sup>, and the molecules were evident after the subsequent Al<sub>2</sub>O<sub>3</sub> deposition process.<sup>25</sup> The attachment of Ru<sub>2</sub> on the SiO<sub>2</sub> surface has been characterized by using the same techniques (Supporting Information). XPS results from the Ru<sub>2</sub>-attached SiO<sub>2</sub>/Si samples clearly show the Ru 3p and Ru 3d peaks, indicating the presence of the Ru<sub>2</sub> SAM on the SiO<sub>2</sub> surface (Figure S1, Supporting Information). CV of the electrolyte-Ru<sub>2</sub>-oxidesilicon capacitor structure shows two pairs of oxidation/ reduction peaks (Figure S3, Supporting Information). The peaks are associated with the redox behavior of the two Ru redox centers within Ru<sub>2</sub>, in which the electrons are stored (reduction) or removed (oxidation) from the molecules. The peak separation is due to the SiO<sub>2</sub> tunneling barrier and the linker part of the molecule. Similarly, the surface coverage



Figure 3. TEM image of the cross section of a ferrocene molecular flash memory device. The red dashed line indicates the ferroceneembedded  $Al_2O_3$  region. The inset shows the cross section of the nanowire channel, with the SiO<sub>2</sub> layer indicated by the dashed line.

density can be calculated, and was estimated to be  $2.54\times10^{13}$   $cm^{-2}.$ 

Schottky-barrier p-type MOSFET characteristics have been observed for the Si nanowire molecular flash memory cells as the source/drain (S/D) was engineered as Schottky junction.<sup>20</sup> Figure 4a and 4b show the output characteristics, drain current  $(I_{DS})$  vs drain voltage  $(V_{DS})$ , of a typical ferrocene molecular flash in linear and logarithmic scale, respectively. The  $I_{DS}-V_{DS}$ curves are smooth and well-saturated, showing negligible contact resistance. The leakage-affected region and the weak, moderate and strong inversion operation regions were clearly shown in Figure 4b. In the weak inversion region, the drain current increased exponentially with gate voltage  $(V_{GS})$  and was saturated at  $3\phi_t$  ( $\approx 78$  mV at room temperature), where  $\phi_t$  is the thermal voltage, indicating the molecular flash memory operates like an ideal conventional MOSFET. Transfer characteristics of ferrocene and Ru<sub>2</sub> molecular flash memory were shown in Figure 4c and 4d, respectively. Counterclockwise hysteresis loops were observed at different gate voltage sweep ranges for both devices, suggesting the charge trapping mechanism. The memory window started to appear at gate voltage as low as 3 V, and increased to sufficiently large with >10 V gate voltage sweep range. The log-scale of the transfer characteristics of the molecular memory are shown in the insets in Figure 4c and 4d. Clear Off states were observed, and the On/Off ratio was as high as  $\sim 10^7$ . Figure 4e shows the  $I_{\text{DS}}\text{-}V_{\text{GS}}$  curves of the reference sample (without molecules) at the same V<sub>GS</sub> sweep ranges, and a negligible memory window was observed. Thus, the possibility of charge storage in the Al<sub>2</sub>O<sub>3</sub> gate dielectric traps can be ruled out.

The P/E characteristics of the molecular memory (ferrocene) are shown in Figure 5a and 5b, demonstrated by the threshold voltage shift ( $\Delta V_{Th}$ ) under different P/E gate voltage pulses. The P/E operations were performed by applying top gate voltage pulses while the substrate, source and drain electrodes were all grounded. As shown in Figure 5a,  $I_{DS}-V_{GS}$ curves were swept after applying +10 V programming gate voltage pulses with increasing pulse width. The threshold voltage showed a clear shift toward the positive direction, indicating the electrons were injected from the Si nanowire through the SiO<sub>2</sub> and stored in the redox centers of the ferrocene molecular layer. Subsequently, erasing operations were performed with -10 V gate voltages with increasing pulse width, as demonstrated in Figure 5b. The back shifting of the threshold voltage toward the negative direction suggests hole injection from the Si nanowire during the erasing operations. The P/E speed characterizations of the ferrocene and Ru<sub>2</sub> molecular memory devices were summarized in Figure 5c and 5d, using  $\pm 8$  V and  $\pm 10$  V P/E gate voltages, respectively. Both molecular memory devices showed fast P/E speed, which arises from the intrinsic fast speed of the charging behavior of the redox centers in these molecules. Careful comparison of the timing of the programming and erasing operations indicates that  $V_{Th}$  shifts are not symmetric, with the erasing -10 V bias having a noticeable shift at shorter times than the programming +10 V bias. We attribute the faster erasing speed to the more favorable hole injection in the Si/SiO<sub>2</sub>/molecule/Al<sub>2</sub>O<sub>3</sub>/gate system largely because of the charging at the molecule/Al<sub>2</sub>O<sub>3</sub> interface states. As discussed above, traps in the Al<sub>2</sub>O<sub>3</sub> dielectric has been ruled out from the possible charge-storage locations based on measurements of our control devices. Therefore, the injected charges can be stored at the molecule redox centers and the molecule/Al<sub>2</sub>O<sub>3</sub> interface traps, which might be due to the natural property of the molecule and dielectric, or introduced during the SAM formation process.<sup>12,27</sup> Figure 6 shows the band diagrams for the Si/SiO<sub>2</sub>/ferrocene/Al<sub>2</sub>O<sub>3</sub>/gate and Si/SiO<sub>2</sub>/Ru<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/gate structures. The highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) for  $Ru_2$  were electrochemically measured and determined to be -5.12 eV/-3.84 eV.<sup>24,28</sup> The HOMO/ LUMO level energies of ferrocene were estimated using a similar method, and were determined to be -5.13 eV/-0.63eV.  $^{29,30}$  The charge neutrality level (CNL) of  $Al_2O_3$  deposited by ALD is -5.2 eV, which can be taken as a local Fermi level of the interface states.<sup>12,31,32</sup> The barrier for electron injection from the Si nanowire can be approximated as the extra energy for electrons to get into the LUMO as  $E_{LUMO} - E_{C}$ , which gives 2.35 eV for ferrocene and 0.23 eV for  $Ru_2$  (E<sub>C</sub> is the Si conduction band edge). The injected electrons will be relaxed into interface states surrounding the CNL due to the lower energy level. On the other hand, the barrier for holes to be injected into the HOMO is  $E_V - E_{HOMO}$  ( $E_V$  is the Si valence band edge), which yields -0.66 eV for ferrocene and -0.05 eV for Ru<sub>2</sub>. Therefore, the energetics of the band alignment indicate hole injection is more favorable than the electron injection.

The charge storage in the interface states can also be derived from the transfer characteristics during P/E operations. The subthreshold slope (S) of the molecular memory after each P/Eoperation can be estimated by using the following equation:

$$S = \ln 10 \frac{kT}{q} \left( 1 + \frac{C_{\text{ch-gnd}} + C_{\text{it}}}{C_{\text{ox}}} \right)$$
(1)

where  $C_{\text{ch-gnd}}$  is the capacitance between the nanowire channel which is in the weak inversion region and ground,  $C_{\text{it}}$  is the interface state capacitance, and  $C_{\text{ox}}$  is the capacitance of the gate dielectric, respectively.<sup>33</sup> For the ferrocene flash memory, the S extracted from the  $I_{\text{DS}}$ – $V_{\text{GS}}$  curves in Figure 5a underwent a slight increase during the accumulative programming process from  $\approx 368 \text{ mV/dec}$  at the fresh state to  $\approx 389 \text{ mV/dec}$  after a + 10 V, 1 s gate voltage stressing. The following accumulative erasing operations (Figure 5b) reversely decreases the S from  $\approx 382 \text{ mV/dec}$  at the programmed state to  $\approx 355 \text{ mV/dec}$  after

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**Figure 4.** (a) Linear and (b) log-scale output characteristics of ferrocene molecular memory with  $V_{GS}$  varying from 0.4 V to -4.2 V, with steps of -0.2 V. (c) Transfer characteristics of ferrocene flash memory at gate voltage sweep ranges of  $\pm 4$  V,  $\pm 6$  V,  $\pm 8$  V,  $\pm 10$  V, and  $\pm 12$  V, respectively. The arrows indicate the directions.  $V_{DS}$  was set to -50 mV. Inset: transfer characteristics in log-scale. (d) Transfer characteristics of Ru<sub>2</sub> molecular memory at gate voltage sweep ranges of  $\pm 3$  V,  $\pm 5$  V,  $\pm 7$  V,  $\pm 9$  V, and  $\pm 11$  V, respectively.  $V_{DS}$  was set to -50 mV. Inset: transfer characteristics in log-scale. (e)  $I_{DS}$ -V<sub>GS</sub> of the reference sample at gate voltage sweep ranges of  $\pm 4$  V,  $\pm 6$  V,  $\pm 8$  V, and  $\pm 10$  V, respectively.

-10 V, 1 s stressing. The Ru<sub>2</sub> flash memory showed a similar behavior. Assuming C<sub>ch-gnd</sub> and C<sub>ox</sub> remain unchanged during the P/E operations, the change in S is likely due to the molecule/Al<sub>2</sub>O<sub>3</sub> interface state charging of electrons and holes during the P/E operations, though the amount of charge is very small even at  $\pm 10$  V, 1 s stressing.

Figure 7a shows the  $\Delta V_{\text{Th}}$  of the ferrocene molecular memory and the reference sample as a function of applied P/E voltages with the P/E pulses width set to 500  $\mu$ s. Increasing P/ E voltage caused a very small  $\Delta V_{\text{Th}}$  for the reference sample, which further supports the dominant charge-storage mechanism to be molecular rather than the solely traps within the Al<sub>2</sub>O<sub>3</sub> gate dielectric or the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> interface. For the ferrocene molecular memory, a large  $\Delta V_{\text{Th}}$  and a clear staircase behavior have been observed, demonstrating discrete energy levels corresponding to various molecular orbitals. The hole injection leads to a clear  $\Delta V_{\text{Th}}$  starting at  $\leftarrow 6$  V gate voltage, while a minimum gate voltage of +8 V is required for electron injection to show a clear  $\Delta V_{\text{Th}}$ . This anisotropy in the  $\Delta V_{\text{Th}}$  is partly due to the more preferred storage of holes than electrons at the ferrocene/Al<sub>2</sub>O<sub>3</sub> interface, as discussed previously. With increasing P/E voltages, the ferrocene molecular memory showed increasing  $\Delta V_{\rm Th}$  until final saturation at ~ ±26 V, suggesting that all of the available redox centers in the ferrocene layer have been occupied by charge. With this saturation condition, we can calculate the charging density in the SAM by using the following equation:

$$\Delta V_{\rm Th} = q \cdot N \cdot \left( \frac{1}{C_{\rm T}} + \frac{1}{C_{\rm link}} \right) = q \cdot N \cdot \left( \frac{\ln\left(\frac{t_{\rm rout}}{t_{\rm Tin}}\right)}{2\pi\varepsilon_0\varepsilon_T L} + \frac{\ln\left(\frac{t_{\rm link-out}}{t_{\rm link-in}}\right)}{2\pi\varepsilon_0\varepsilon_{\rm link} L} \right)$$
(2)

where q is the elementary charge, N is the total charge stored in the redox centers,  $C_{\rm T}$  and  $C_{\rm link}$  are capacitance of the tunnel oxide and the linker part of ferrocene;  $t_{\rm Tout}$ ,  $t_{\rm Tin}$ ,  $t_{\rm link-out}$ , and  $t_{\rm link-in}$  are the distances from the center of the Si nanowire to the outside and inside surfaces of the tunnel oxide layer and the ferrocene linker;  $\varepsilon_{\rm T}$  and  $\varepsilon_{\rm link}$  are the dielectric constants of SiO<sub>2</sub>



Figure 5. (a) Programming and (b) erasing operations of the ferrocene molecular memory under accumulative rectangular P/E gate voltage pulses. The gate voltage was set to  $\pm 10$  V with increasing pulse width. V<sub>DS</sub> was set to -50 mV. (c and d) illustrate the P/E speed characterization of ferrocene and Ru<sub>2</sub> flash memory, respectively.



Figure 6. Schematic band diagram of the (a) p-Si/SiO<sub>2</sub>/ferrocene/Al<sub>2</sub>O<sub>3</sub>/gate and (b) p-Si/SiO<sub>2</sub>/Ru<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/gate systems.

and the ferrocene linker, and *L* is the channel length. The saturated  $\Delta V_{\rm Th}$  obtained from Figure 7a ( $\approx$ 1.69 V) and the presumed ferrocene linker with length of 0.5 nm and a dielectric constant of 2.5 can be used to calculate the charge density of the SAM. The calculated charge density is around 6.96  $\times$  10<sup>12</sup> cm<sup>-2</sup>, which is comparable to the results obtained from the capacitor structure.<sup>25</sup> Such a high charge-storage density in a SAM is very important for on-chip memory applications requiring high integration density of nonvolatile memory.

Two-step charge-storage behavior was observed in the Ru<sub>2</sub> molecular flash memory, due to the two redox states in the Ru<sub>2</sub> molecules which can exhibit stable and distinct charged states at different voltage level. As shown in Figure 7b, with increasing programming gate voltage, the first step charged state was observed at 10 V, with 0.8 V  $\Delta V_{\text{Th}}$ , indicating that the Ru<sub>2</sub> redox centers with lower voltage levels have been occupied by electrons. With increasing programming voltage, the second charged state step was observed beyond  $V_{\text{GS}} = 14$  V with a saturated  $\Delta V_{\text{Th}}$  of 1.95 V. This suggests that all the Ru<sub>2</sub> redox centers in the molecules have been filled with injected

electrons. The overall charging density of Ru<sub>2</sub> SAM can be calculated with eq 2 by using the  $\Delta V_{\rm Th}$  at the second charged state to yield the charging density of  $1.12 \times 10^{13}$  cm<sup>-2</sup>. It is worth mentioning that even though the charging density of the Ru<sub>2</sub> molecules is about half of the coverage density obtained from the CV measurement (similar for ferrocene), effective memory characteristics can still been achieved. Such discrete charging behavior in Ru<sub>2</sub> molecules with multiple redox centers is very attractive for discrete multi-bit memory application.

The room temperature retention properties of the ferrocene and Ru<sub>2</sub> molecular memory were demonstrated in Figure 7c and 7d, respectively. The devices were initially programmed/ erased by  $\pm 10$  V gate voltage with 500 and 100  $\mu$ s pulse width. Good charge retention characteristics were observed, with a projected 10-year memory window showing only ~20% charge loss for both devices. The good retention is due to the intrinsic stable redox behavior of the molecules and the high-quality tunnel oxide with clean solid/molecule and dielectric interfaces by using the self-alignment fabrication process. This further supports the mechanism of dominant charge storage located in the redox centers of the molecules instead of the molecule/



**Figure 7.**  $\Delta V_{\text{Th}}$  of (a) ferrocene flash memory and reference sample and (b) Ru<sub>2</sub> flash memory as a function of P/E voltage with 500  $\mu$ s pulse width and increasing pulse height. Room temperature retention characteristics of (c) ferrocene and (d) Ru<sub>2</sub> flash memory. The devices were initially programmed/erased by ±10 V gate voltage pulses with 500 and 100  $\mu$ s pulse width, respectively. A 10-year memory window was projected. Endurance property of (e) ferrocene and (f) Ru<sub>2</sub> flash memory. ±10 V gate voltage pulses with 500 and 100  $\mu$ s pulse width were applied. Negligible memory window degradation was observed after 10<sup>9</sup> P/E cycles.

Al<sub>2</sub>O<sub>3</sub> interface states, since the recovery process of the interface states is quite fast leading to a poor retention. The endurance properties of the molecular memory were characterized by applying  $\pm 10$  V P/E gate voltages with 500 and 100  $\mu$ s pulse width. As shown in Figure 7e and 7f, both devices showed excellent endurance characteristics, with negligible memory window degradation after 10<sup>8</sup> P/E cycles by applying 500  $\mu$ s P/E voltages. With 100  $\mu$ s P/E voltages, the device still functions perfectly even after 10<sup>9</sup> P/E cycles. This is about 10,000 times better than that of the conventional floating gate memory (10<sup>5</sup> cycles). Such excellent endurance characteristics result from the excellent reliability of the redox properties of the ferrocene and Ru<sub>2</sub> molecules, which makes them very attractive for future fast speed, high-endurance and high-density on-chip nonvolatile memory applications.

### CONCLUSION

In summary, novel high-performance Si nanowire FET based molecular nonvolatile flash memory has been fabricated and studied. Excellent memory characteristics have been obtained, such as fast P/E speed, large memory window, and sufficient

charge trapping density. The charge-storage mechanism has been investigated in these devices. The injected charges are mainly located in the redox centers of the molecules, with only a trace amount stored in the molecule/Al<sub>2</sub>O<sub>3</sub> interface traps. Discrete charge storage has been achieved in Ru<sub>2</sub> molecular flash, enabling discrete multi-bit memory application. Good charge retention and excellent endurance properties have been obtained. Negligible memory window degradation was observed after 10<sup>9</sup> P/E cycles. These excellent characteristics are inherently the result of both the good intrinsic charging properties of the redox-active molecules and the protection of the molecules in the device structure obtained by the selfalignment fabrication. Such high-performance molecular flash memory is very promising for future on-chip nonvolatile memory applications with fast speed, low power, high density, and excellent endurance.

#### EXPERIMENTAL SECTION

Self-aligned Si nanowire FET platform preparation. A 300 nm  $SiO_2$  was first grown on a highly doped p-type Si (100) wafer by dry oxidization. Then a thin film of Au catalyst (2–3 nm) was deposited

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onto a patterned area predefined by photolithography. Next, the Si nanowires were grown from the catalyst in a low-pressure chemical vapor deposition (LPCVD) furnace at 440 °C for 2 h with an ambient SiH<sub>4</sub> stream under a pressure of 500 mTorr. The Si nanowires growth is the conventional vapor-liquid-solid (VLS) mechanism, yielding typical lengths of 20  $\mu$ m and a 20 nm diameter. Immediately after the growth step, the Si nanowires were oxidized at 750 °C for 30 min to form a  $\approx 3$  nm SiO<sub>2</sub> on which the SAM will be formed. This thin layer of SiO<sub>2</sub> was also expected to provide a good interface between the Si nanowire and the Al2O3-based gate dielectric which was deposited after the SAM was formed. The next step is to pattern the source/ drain (S/D) electrodes with photolithography. A 2% HF wet etch was applied to remove the oxide from the Si nanowire at the patterned S/ D area immediately before the 5/100 (unit: nm) Ti/Pt was deposited by e-beam evaporation and lift-off process to form the Schottky barrier S/D contacts. The channel length between the S/D electrodes was controlled to be 6  $\mu$ m.

Synthesis of  $Ru_2(ap)_4(C_2C_6H_4P(O)(OH)_2)$  molecule. Precursor  $Ru_2(ap)_4(C_2C_6H_4P(O)(O^{t}Bu)_2)$  was prepared according to Reference [24].  $Ru_2(ap)_4(C_2C_6H_4P(O)(OH)_2)$  was obtained by treating the precursor with bromotrimethylsilane/Et<sub>3</sub>N in large excess, and recrystallized from THF/hexanes.

**SAM attachment and final device.** The SAMs of ferrocene and Ru<sub>2</sub> formed on SiO<sub>2</sub>/Si nanowire channel were then prepared by placing droplets of a solution of dichloromethane with 3-mM ferrocene and 2-mM Ru<sub>2</sub> on active areas separately. Each drop was in place for 3–4 min and the samples were held at 100 °C in an N<sub>2</sub> environment during the attachment process. Saturated SAMs will be formed after ~30 min. After the self-assembly process, dichloromethane was used to rinse the wafers in order to remove any residual molecules that are not bonded to the SiO<sub>2</sub> surface. Then, the samples were immediately loaded into the atomic layer deposition (ALD) chamber. A layer of 25 nm Al<sub>2</sub>O<sub>3</sub> was deposited with trimethyl aluminum (TMA) and H<sub>2</sub>O as precursors at 100 °C. Finally, a 100 nm Pd top gate was formed with the same photolithographic and lift-off processes as S/D electrodes. A reference sample without redox molecules was fabricated at the same time for comparison.

## ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b08517.

XPS and CV sample preparation and characterization of the Ru<sub>2</sub> molecule. (PDF)

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# Notes

The authors declare no competing financial interest.

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