Published in final edited form as:

J Phys Condens Matter. 2016 March 9; 28(9): 094009. doi:10.1088/0953-8984/28/9/094009.

Non-volatile Memory Devices with Redox-active Diruthenium Molecular Compound

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Abstract

Reduction-oxidation (redox) active molecules hold potential for memory devices due to their many unique properties. We report the use of a novel diruthenium-based redox molecule incorporated into a non-volatile Flash-based memory device architecture. The memory capacitor device structure consists of a Pd/Al₂O₃/molecule/SiO₂/Si structure. The bulky ruthenium redox molecule is attached to the surface by using a “click” reaction and the monolayer structure is characterized by X-ray photoelectron spectroscopy to verify the Ru attachment and molecular density. The “click” reaction is particularly advantageous for memory applications because of (1) ease of chemical design and synthesis, and (2) provides an additional spatial barrier between the oxide/silicon to the diruthenium molecule. Ultraviolet photoelectron spectroscopy data identified the energy of the electronic levels of the surface before and after surface modification. The molecular memory devices display an unsaturated charge storage window attributed to the intrinsic properties of the redox-active molecule. Our findings demonstrate the strengths and challenges with integrating molecular layers within solid-state devices, which will influence the future design of molecular memory devices.

I. Introduction

With the explosive demand for personal and portable computing devices such as phones, laptops, and tablets within the last decade, the growth in Flash-based memory has also increased dramatically. Non-volatile Flash memory is essential in the operation of these personal devices and is attractive because the memory state is retained even when power is no longer supplied. As the demand for these devices continues to grow, substantial dimensional scaling of memory components faces many critical challenges as there are serious material limitations. One of the device layers essential to memory retention is the floating gate or charge trapping layer,¹ which in current commercial Flash memory typically consists of polycrystalline silicon as the conductive floating gate. To scale the charge trapping layer to nanometer dimensions, it is appealing to use a discrete charge storage layer

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that is based on nanocrystals,^{2,3,4} nanoparticles,⁵ nanographene,⁶ or organic molecules.^{7, 8, 9,10,11}

Organic molecules are appealing for a variety of reasons due to their nanoscale features and tunable electronic properties. Incorporating molecules lend to bottom-up assembly which is compatible with commercial fabrication and device miniaturization. Molecular solids contain frontier bonding orbitals that are involved with charge processes, which are discrete and localized on the atoms itself. The latter property is advantageous in the development for applications in Flash memory. The highest occupied molecular orbital (HOMO) energetic position is tunable since it is dictated by the chemical composition and nature of the bonding, which can be altered by chemical synthetic design and allows for “tailor-made” electronic properties. Molecules are able to hold high charge densities (one or more charges per molecule), making molecular layers particularly appealing for high-density memory storage applications. Finally, a molecule is the smallest engineered unit of fixed elemental composition with footprints on the order of nanometers and the size of organic molecules is compatible with dimensional scaling of semiconductor technology. Thus, Flash memory can take advantage of the size and discrete energy levels of organic molecules as charge trapping sites in order to meet the critical dimensional needs of the Si-based semiconductor manufacturers.

Molecules that undergo reduction-oxidation (redox) reactions are attractive as the charge trapping sites because they can access additional charged states when the system’s potential is altered. Redox molecules for this application hold promise and have been demonstrated with fullerenes,^{9, 12, 10} ferrocenes,^{8, 1113} and porphyrins.⁸ The redox-active molecule diruthenium(II,III)tetrakis(2-anilinoipyridinate) (now referred to as Ru₂, see Figure 1c) offers accessibility to multiple redox states^{14, 15} and can be potentially exploited for multilevel programmability. Other redox-active molecules must be explored to further understand the connection between solution phase redox-activity intrinsic to the molecule, and the ultimate charge-storage properties that the molecule exhibits when integrated within a solid-state device.

Molecular attachment by click chemistry eases constraints and limitations on chemical synthesis, and provides a platform for versatility in self-assembly. Self-assembly of organic molecules onto surfaces is no longer limited to soluble thiol- or phosphonic acid-bearing molecules which substantially eases synthetic efforts. Click chemistry provides a modular route to build up tailored organic molecular layers for specific purposes, such as biomedical applications¹⁶ and electrochemical reduction of carbon dioxide.¹⁷ In this instance, a molecular layer bearing a terminal azide functional group is required as the base layer to which Ru₂ can be “clicked” onto. Here, we apply this attachment technique to capacitor-based memory devices which allows the attachment of Ru₂. In addition to lending itself for modular attachment, the bottom molecular layer also adds additional “length” between redox active molecule and silicon substrate, which is good for electrical isolation. This platform allows us to investigate the impact of a redox-active molecule that has been integrated in a solid-state device. We find that the Ru₂ incorporated layer plays a dominant role in the charge storage, by providing charge trapping sites at the Ru₂/Al₂O₃ interface.

II. Experimental Methods

The metal-oxide-semiconductor (MOS) capacitor structure, used in our Flash memory devices (see Figure 1a) was fabricated with Ru₂ redox-active molecules as the charge trapping layer (see Figure 1b). The molecular memory capacitor structure process has been reported before,¹¹ but we briefly describe it here. Silicon dioxide (110 nm) is thermally grown on a lightly p-doped Si (100) substrate followed by the definition and etching of square active areas (100 μ m wide) using standard photolithography techniques. Next, a thin SiO₂ (1.5 nm) is grown in the Si-exposed active area by rapid thermal oxidation and serves as the tunneling oxide. The diruthenium molecule is attached by “click” chemistry onto the tunneling oxide layer, and the details of the attachment are described previously.¹⁸ The molecular layer is covered with Al₂O₃ (20 nm), as the control or blocking oxide, formed by atomic layer deposition at 100 °C with trimethyl aluminium (TMA) and H₂O as precursors. The alumina layer should prevent hybridization between the molecule and metal gate and this should aid in charge retention. Cross-sectional Scanning Transmission Electron Microscopy (STEM) with a high-angle annular dark field (HAADF) detector provides imaging of the molecular layer interfaced with Al₂O₃ and SiO₂ in Figure 1c. Finally, palladium (105 nm) is deposited as the top gate.

All electrical characterization was measured in a light sealed, commercial probe station. Bias was applied to the metal gate (i.e., palladium contact) while the silicon substrate was grounded for all electrical measurements. To test the memory retention of the molecular memory devices, capacitance-voltage measurements were performed at various frequencies by using an Agilent E4980A LCR meter.¹⁹ Pulsed measurements were performed with an Agilent 4156 Semiconductor Parameter Analyzer, and program-erase endurance tests were performed with a Hewlett Packard 33120A waveform generator.

To confirm the attachment of the molecular layer onto SiO₂, both the azide-containing molecular layer (azidoundecyltrimethoxysilane, AUS, “before click”) and the Ru₂ molecules (“after click”) were investigated by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra instrument equipped with monochromatized Al K α photons. Ultraviolet photoelectron spectroscopy (UPS) using He I excitation and a –5.5 V bias applied to the sample surface was also performed in the same instrument to determine the energetic position of the highest occupied system orbitals (HOSO) of the molecular layers and the work function of the modified surfaces.

III. Results and Discussion

Monolayers were made by utilizing “click” chemistry to attach Ru₂ to a AUS monolayer on SiO₂/Si.¹⁸ Attachment of the Ru₂ molecule by “click” chemistry is evaluated by XPS measurements to verify the molecular density and chemical state of the molecules present. Figure 2 presents XPS spectra obtained from the bare silicon oxide substrate, the AUS terminated SiO₂/Si surface (before “click”), and the Ru₂ terminated SiO₂ surface (after “click”). Before “click” attachment of Ru₂, there is a strong C 1s signal which is attributed to the AUS molecule attachment to the SiO₂/Si surface (Figure 2a, in black) which is significantly stronger than the adventitious carbon present on the bare SiO₂/Si substrate

(Figure 2a, in blue). The C 1s emission at 285.1 eV and 286.7 eV correspond to the aliphatic backbone contribution²⁰ of the AUS layer. The presence of the azide-containing molecular layer is also confirmed in the N 1s spectrum (not shown). After “click” attachment of the Ru₂ molecule, Ru 3d_{5/2} and Ru 3p spectral features are detected at the surface. With the attachment of Ru₂, the C 1s spectral shape is modified by the the new carbon-containing components present in the Ru₂ molecule, and a new spectral feature corresponding to the Ru 3d_{5/2} appears (281.4 eV). The Ru 3d_{3/2} is not discernible as it overlaps with the more intense main C 1s region. Additional evidence of the successful Ru₂ attachment by “click” chemistry is directly confirmed in the Ru 3p spectrum (Figure 2b, in red) which previously had no spectral features in the “before click” spectrum. Based on our earlier procedure¹⁸ to estimate the Ru₂ density on the surface from XPS data, we determine the molecular density of about one Ru₂ molecule attached to every 5 AUS molecules on the SiO₂/Si surface. Furthermore, the density of Ru₂ molecules on the SiO₂/Si substrate can be estimated by using the Ru 3d and Si 2p spectral lines. We find that there are about 0.26 Ru₂ molecules attached per nm². Thus, we can confirm that Ru₂ is directly on the surface and attached to the AUS layer, and at an optimal coverage to serve as a charge storage layer for molecular memory devices.

The electrical properties of the Ru₂ molecular layer were examined with high-frequency (HF) capacitance voltage (CV) measurements as shown in Figure 3. A capacitor structure consisting of 20 nm of Al₂O₃ and a palladium top gate (as shown in Figure 1) was characterized at 1 MHz with very different results obtained for the no molecule control and the Ru₂-containing structure, as shown in Figure 3a and 3b. The CV was measured by sweeping the gate bias from accumulation to inversion (negative to positive gate bias) for hole charging and then back, from inversion to accumulation (positive to negative gate bias) for electron charging. From the CV measurement, the flatband voltage (V_{FB}) can be estimated and V_{FB} position is sensitive to fixed and mobile charge carriers between the gate and the semiconductor layer. The V_{FB} physically corresponds to the bias condition where the silicon valence and conduction bands at the Si-SiO₂ interface are flat, and here it is graphically estimated in the depletion region of the CV curve where the slope is at a maximum. There are two observations within the data as a function of sweeping the gate voltage: the hysteresis width (V_{FB}) and its asymmetric widening (as denoted as V_{FB_left} and V_{FB_right} in Figure 3c). Both of these effects are observed for the Ru₂-containing device and the no-molecule control device, but these effects are much greater in magnitude for the molecule-containing device (as can be directly compared in Figure 3c). The Ru₂ containing device shows a much larger V_{FB} indicating the device structure containing the molecular layer is more active to charge trapping. The flatband positions of the molecular memory device are shown in Figure 3c, and it can be seen that it does not evolve symmetrically (i.e., the magnitude of the left and right derived V_{FB} differs) with gate bias sweep direction. The V_{FB_right} , derived from the backwards sweep which goes from positive to negative gate bias, is more sensitive than V_{FB_left} indicating a preference for trapped electrons, rather than holes. This property has also been observed in other molecular-based charge trapping memory devices,^{9, 21, 6} and can be explained by asymmetric energy level alignment of the HOSO or lowest unoccupied system orbital (LUSO) interfaced with the gate dielectric.

The second effect apparent in the data shown in Figure 3a and 3b is the width of the hysteresis curve (V_{FB}), or the memory window. First, the control device contains no observable hysteresis until ± 11 V where a relatively small hysteresis is observed with a memory window of about 1 V, consistent with field-induced damage of the dielectric and in agreement with control devices previously reported.¹¹ The Ru₂ containing devices exhibit a hysteresis at lower gate voltages and the width (or memory window) is greater, despite the added thickness the molecular layer presents. When the gate voltage sweep is increased to -11 V and $+11$ V, the memory window increases to ~ 4.0 V. The amount of charge stored (Q) within the hysteresis loop (i.e., memory window) can be estimated by using the following relation:

$$Q = C_i \Delta V_{FB} \quad (1)$$

where C_i is the capacitance at strong accumulation (26.5 pF). The charge stored as a function of the maximum electric field applied across the memory device is shown in Figure 3d. The charge within the memory window does not saturate which indicates that more charge could still be stored in the Ru₂-containing memory device and the charge storing sites provided by the molecules have not been exhausted. At ± 11 V (or an electric field of 4.23×10^8 V/m), the charge density is about 1.05×10^{-6} per cm² and corresponds to 6.55×10^{12} electrons stored per cm². Furthermore, the stored electron density can be compared to the Ru₂ molecular density, and we find that approximately 1 electron is stored for every 4 Ru₂ molecules present (at ± 11 V) which further supports our conclusion that the charge storage sites on the molecule (or Ru₂/Al₂O₃ interface) are not exhausted. The CV hysteresis is sensitive to changes in the amount of charge between the blocking and tunneling oxide layers, and the charge can either be stored in dielectric traps of the Al₂O₃, traps near the Ru₂/Al₂O₃ interface, or the Ru₂ itself. The observation of increased hysteresis for the Ru₂ memory structure suggests that the molecular layer is playing an integral part in storing the charge. The memory window for the Ru₂ containing molecules are observed at much lower gate voltages, despite being an effectively thicker dielectric layer (when compared to the no molecule control). A similar memory window and response has been reported for a different redox molecule in an identical capacitor memory structure.¹¹ Therefore, we attribute the memory window observed in the Ru-containing device due to the presence of the molecular layer itself. Thus, we surmise that the molecular layer stores electrons when the electron tunnels from the silicon layer to the molecular layer (electron charging), and an electron tunneling back to the silicon layer (hole charging).

Program (P) and erase (E) operations on the diruthenium-containing memory devices were performed for a variety of pulse widths and are shown in Figure 4. To program the device, a rectangular $+10$ V pulse was applied to the gate for a specified duration (pulse width), while a -10 V pulse was applied to erase the device (also for a specified duration). After programming (erasing) the device, HF CV measurements at 1 MHz were performed where the gate bias is swept from positive (negative) bias to negative (positive) bias in order to study the electron (hole) injection into the Ru₂ molecular layer to monitor the V_{FB} compared to a non-pulsed measurement (referred to as “0 s” in Figure 4). For the P/E operation, the change in V_{FB} can be observed with increasing pulse width, where a pulse

width of 1 ms is required to program and erase the device at ± 10 V. Aside from the VFB shifting, the C-V curve does not change with varying P/E pulse widths which is expected. The P/E widths necessary for this Ru₂ memory device are comparable to those reported of other molecular-based memory devices that incorporate polymers²² and porphyrins.²¹ In our previous study with ferrocenylethanol directly attached to the SiO₂/Si, the P/E speeds were relatively fast with responses in the order of microseconds.¹¹ Pro *et al* used density functional theory to calculate the energetic barriers for electron transfer between Si and ferrocene in different attachment schemes: (1) directly attached and (2) attached by “click” chemistry.¹³ Those authors concluded that there was a larger energetic barrier to transfer electrons between the ferrocene and Si when the ferrocene had an additional linker (e.g. an AUS layer).¹³ Our result and results in the literature suggest that the millisecond pulse widths required to program and erase charge are dependent on the size of the molecule and the distance to the Si layer. The distribution of V_{FB} for the erase function is relatively narrow (Figure 4b) when compared to the V_{FB} of the program function (Figure 4a), and this indicates that the Ru₂ memory devices have faster programming response than erasing response. The physical origination in program and erase times could be due to the difference in the density of traps for holes and electrons within the molecular layer (or at the molecule-Al₂O₃ interface) and/or the relative energetic positions of the molecular orbitals with respect to the band edges of the inorganic layers. These differences in speed are suitable for Flash memory applications since programming is done as individual bytes, while erasing is applied to blocks or sectors. We also note that even for 1 second pulse lengths, the shift in the V_{FB} does not appear to saturate for either program or erase operations, which suggests that the Ru₂ molecular layer provides more than sufficient charge trapping sites. This finding is also in agreement with what we concluded earlier that at these gate biases, the charge sites provided by the Ru₂ molecular layer have not been exhausted.

To test the potential applicability of Ru₂-based memory devices, P/E endurance and retention measurements were performed and shown in Figure 5. P/E cycles were performed by using a function generator with a square wave-type function with a pulse width of 1 ms (peak height +10 V for programming, -10 V for erasing). After a number of P/E cycles, pulsed HF CV measurements were performed to monitor the relative shift of the V_{FB} . After 100,000 P/E cycles, the memory window is about 1.98 V (in Figure 5a). It is about 4% smaller when compared to the characteristics which can be attributed to the charge retention of the molecules or at the molecule/Al₂O₃ interface combined with the good quality of the tunneling oxide and blocking oxide layers. The retention characteristics of another Ru₂-containing device are displayed in Figure 5b. At close to 10⁴ s, the memory window shrinks by about 20% compared to the initial measurement at about 10¹ s. This retention capability is comparable to our previous report of a ferrocene-based memory device which is sufficient for non-volatile memory applications.¹¹ It is likely that the original AUS layer adds additional spatial and insulating functionality which separates the Ru₂ molecule from the tunneling SiO₂ layer, which likely helps to prevent charge loss.

Insight into how the Ru₂ memory device operates is gained through measuring the relevant band (or orbital) energy levels involved with charge transport, and the proposed band diagram is shown in Figure 6. UPS measurements provide insight into the shallow occupied energy levels which contribute to the hole transport in the memory device. The unoccupied

energy levels (i.e. conduction band levels) of SiO_2 and Al_2O_3 are taken from literature²³ which were measured from a complementary technique, inverse photoemission (IPES). As we previously reported,¹⁸ the Ru_2 click molecular layer has a favorable HOSO position with respect to the valence band edge of moderately doped Si, and this should aid in the tunneling of holes from the silicon valence band into the Ru_2 HOSO. The lowest unoccupied system orbital (LUSO) of the Ru_2 (assuming the band gap estimated by density functional theory¹⁵) should also be more favorably aligned with the Al_2O_3 conduction band edge versus the SiO_2 conduction band edge and aid in storing electrons at that interface. Thus, the energy alignment provides a strong case that charge trapping within the Ru_2 molecular memory device is likely to be at the Ru_2 - Al_2O_3 interface and thus the Ru_2 plays an essential role to the operation of the memory device.

The “click” reaction provides versatility to making designer molecular interfaces with considerable ease due to its modular approach. However, adding an additional insulating molecular layer as the foundation for “click” reacting Ru_2 , has both positive and negative effects. The AUS layer serves as a spatial insulator between the Ru_2 and the SiO_2/Si which likely aids in the good charge retention in the memory window and endurance characteristics. On the other hand, the AUS layer likely provides an additional energetic barrier for charges to move between the Ru_2 molecule and the Si which was demonstrated in the relatively slow programming-erasing speed. Depending on the application of molecular memory devices, slow programming-erasing speed could be tolerated and then the “click” attachment approach is viable for making customizable molecular interfaces.

IV. Conclusion

We have demonstrated molecular memory-based devices with a redox-active diruthenium compound which are attached via an alkane molecular layer through “click” chemistry. Our approach to attach the Ru_2 molecules by “click” reaction allowed a modular and designer approach to build a molecular-inorganic interface within the memory device. These molecular memory devices display a large memory window in high frequency CV measurements, which can be attributed to the Ru_2 molecules playing an active role as charge traps. The programming and erasing speed are suitable for Flash applications, and can be further improved by tailoring the molecular structure or shortening the distance between the Ru_2 and the Si layer. The viability of hybrid memory devices is demonstrated with the stability of the memory window after endurance testing. Successful demonstration of a Ru_2 memory device is attributed to the Ru_2 molecule, the high-quality Al_2O_3 dielectric layer, and the energy alignment between the Ru_2 and Al_2O_3 which resulted in the favorable charge trapping at the molecular interface. These results provide insight into the design and limitations of molecular layers incorporated within a solid-state device, and will impact the future design considerations of molecular memory devices.

Acknowledgments

We thank Dr. Son Le for fruitful discussions. The memory devices were fabricated in part and TEM imaging were performed at the NIST Center for Nanoscale Science and Technology. The synthetic work at Purdue is supported in part by the National Science Foundation (CHE 1362214).

VI. References

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Figure 1.

Schematic cross-sectional drawing (not to scale) of a (a) prototypical Flash-based memory device, (b) the molecular memory device in a capacitor structure used in this study, and (c) HAADF STEM image of the molecular interface between Al_2O_3 and SiO_2 . An aliphatic linker (AUS) is chemically bonded to the SiO_2 tunneling layer and the Ru_2 layer is chemically tethered to the azide by “click” chemistry. In (d), the chemical structure of the redox-active Ru_2 and the aliphatic AUS are shown, and corresponding molecular cartoons are defined.

Figure 2.

XPS spectra the molecular layer before and after “click” attachment of Ru₂ in the (a) C 1s and Ru 3d regions, and (b) Ru 3p region.

Figure 3.

High frequency (1 MHz) CV measurements of memory device structures (a) with and (b) without diruthenium molecules for different gate voltage sweep ranges, in order to observe the hysteresis. Arrows indicate the sweep direction of the measurement. The position of the flatband voltage (V_{FB}) (c) of the Ru_2 -containing device and the control device extracted from (a) and (b). Estimated charge within the memory window (d) extracted from the data in (a). $V_{\text{FB_left}}$ ($V_{\text{FB_right}}$) denotes the V_{FB} position derived from the initial (backwards) sweep direction, from negative (positive) to positive (negative) gate bias.

Figure 4.

Programming (a) and erasing (b) operations of the Ru₂-containing molecular memory devices. Program and erase functions were performed at +10 V and -10 V, respectively. The pulse width is indicated in the plot.

Figure 5.

Endurance (a) and retention (b) characteristics of the Ru₂-molecular memory device. In (a), the flatband voltage is monitored after P/E (± 10 V, width of 1 ms) cycles. In (b), the gate voltage is ± 10 V with pulse width of 10 ms and 300 ms for P and E, respectively. The devices in (a) and (b) are different, but from the identical device fabrication run. memory window after 10 P/E cycles. The molecular memory device has good endurance

Figure 6.

Proposed band alignment in the actual Ru₂ molecular memory device where the values are derived from our UPS measurements as well as UPS and IPES in the literature. The valence band and HOSO edges are shown as filled rectangles, while the conduction band and LUSO edges are unfilled rectangles. E_{vac} refers to the vacuum level, the Pd work function is shown, and the band gap energy are shown for Si, SiO₂, Ru₂-AUS molecular layer, and Al₂O₃. This diagram is drawn with vacuum level alignment in consideration.