The Cyclic Charging of Reduction-Oxidation Markers in Metal-Oxide-Semiconductor Capacitors

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Abstract:

The study of the cyclic charging of reduction-oxidation (Redox) markers in metal-oxide-semiconductor (MOS) capacitors would allow for the eventual creation of a memory device that contains a molecular component. This molecular component would be a redox organometallic compound such as ferrocene. Redox molecules have naturally occurring discrete energy levels that can store charge. The creation of a device that utilizes the charge-storing capability of these molecules would allow for the creation of a multi-bit memory. The memory created would be able to function at low potentials and be able to undergo trillions of read-write cycles [1].

Experimental Procedure:

For this research project, a functional molecular memory was not obtained. The ultimate goal of this project was to create device that exhibited "Coulomb Staircase" behavior, an indication that the molecule is storing the charge on its discrete energy levels [2,3]. Although a device that exhibits this behavior was not obtained, a great deal of knowledge about the mechanism of molecular memory was obtained.

A basic MOS capacitor with the integration of a redox molecule was fabricated. (See Figure 1.)

First, a 2 nm tunneling oxide of silicon dioxide (SiO_2) was grown on a silicon substrate. Then a self-assembled monolayer (SAM) of benzoic acid and ferrocene was formed. Next a 25 nm control oxide of aluminum oxide (Al_2O_3) was deposited using atomic layer deposition (ALD). A gate metal of 100 nm of chromium (Cr) and 50 nm of aluminum (Al) was deposited. The gate metal was patterned using lithography and etching techniques. The device was annealed to rid the control oxide of interface traps. Finally the device was tested using a capacitance-voltage (CV) meter.

For this experiment, three sets of complete devices were fabricated. The first set was used to determine if the molecule was indeed storing a charge. The second set was used to determine whether a thermal or plasma method of deposition of the control oxide would produce better results. The third and final set was used to determine what annealing temperature would produce the best results.

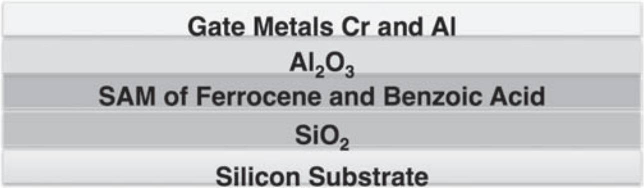

Figure 1: A depiction of the cross-section of the fabricated device.

For trial one, three samples were created: a control sample without a SAM, a benzoic acid only sample with just benzoic acid in the SAM, and a ferrocene/benzoic acid mixture sample with a mixture in the SAM. This experiment was designed to test whether or not a charge was indeed being stored by the molecule and not interface traps. In the control sample, there was no charge storage site because no molecule or intentional dielectric trap was inserted in the gate stack. Both the benzoic acid only and ferrocene/benzoic acid samples exhibited charge storage. The charge storage in the benzoic acid only sample was unexpected because a redox molecule was not present, indicating interface traps in the control oxide. This rendered the data inconclusive as to whether or not the molecule alone was storing a charge since a sample without a molecule was storing a charge. To improve upon this data, it was decided to test whether a thermal or plasma method of deposition for the control oxide would produce better results by reducing interface traps in the control oxide.

For trial two, several process splits were employed to test whether a thermal or plasma method of deposition of the control oxide would produce better results. For this trial, each method of deposition was tested using a control sample against a ferrocene and benzoic acid mixture. In comparing the control samples of this trial, one was able to see that, before annealing, the plasma method of deposition exhibited did not exhibit charge storage (see Figure 3), while the thermal method did exhibit charge storage. The charge storage of the thermal method sample indicated interface traps. From this data, it was determined that the plasma method of deposition produced the best and most consistent results across devices. However, after annealing, the heat sensitive molecules decomposed, resulting in inconsistent charge storage across devices.

For trial three, it was decided to test different annealing temperatures to determine which would produce the best control oxide, but maintain the integrity of the molecules. Three different annealing times and temperatures were tested, 400°C for 30 minutes, 200°C for 60 minutes, and 100°C for 90 minutes. It was determined that annealing at 200°C produced the best results. The electron injection test after annealing at 200°C produced the most consistent charge storage. (See Figure 3.) Annealing at 400°C destroyed the heat sensitive molecules resulting in no charge storage. Annealing at 100°C created more interface traps in the oxide, resulting in inconsistent charge storage. Different ratios of ferrocene to benzoic acid were also tested, but did not result in a significant difference in charge storage.

Results and Future Work:

Although "Coulomb Staircase" behavior was not exhibited by any of the samples, a great deal about the application of redox molecules to a memory device has been learned. The redox molecule can indeed store a charge; however, interface traps in the control oxide layer prevented one from conclusively stating whether or not the molecule alone was storing the charge. To improve the oxide layer, different methods of deposition were tested. It was determined that a plasma method of deposition created a better oxide. Finally, different annealing temperatures were tested to determine how much heat could eliminate the interface traps and leave the molecules intact. It was determined that an annealing temperature of 200°C would produce the best device.

From this information one can perform further testing to try and obtain a working memory device with the integration of a redox molecule. Perhaps adjusting the annealing temperature into finer increments would produce a better device that would exhibit staircase behavior but have no traps. For this research only one type of molecule was used, perhaps a different molecule could withstand the high annealing temperatures. Creating this device would result in a smaller, cheaper, multi-bit memory that can undergo trillions of read-write cycles.

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References:

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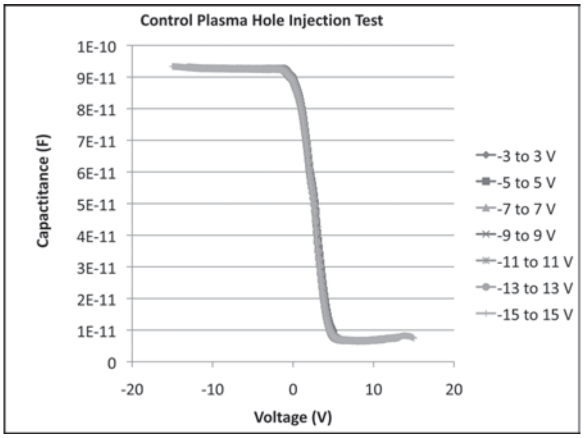

Figure 2: As the testing voltage increases there is no shift, indicative of no charge storage and no interface traps.

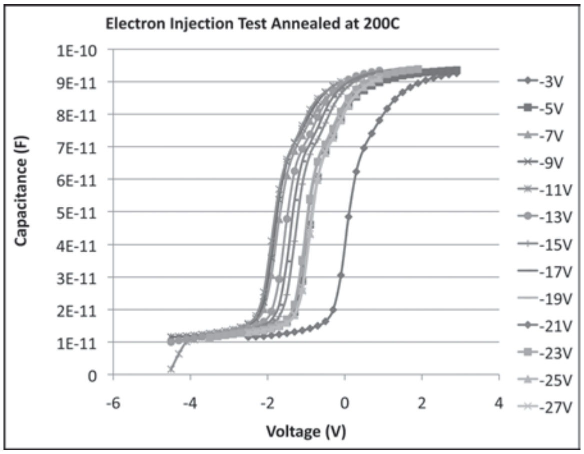

Figure 3: As the testing voltage increases, there is a consistent shift, indicating a stored charge.