I-V Characteristics of Al/HfO2/TaN RRAM Devices

By

Arturo H. Valdivia

A Project

submitted to

Oregon State

University Honors College

in partial fulfillment of

the requirements for

the degree of

Honors Baccalaureate of Science in Chemical Engineering
Honors Baccalaureate of Science in Chemical Engineering Project of Arturo H Valdivia. Student presented June 5, 2013

Approved

____________________________

Major Professor, representing Electrical and Computer Engineering

____________________________

Committee Member, representing Chemical Engineering

____________________________

Committee Member, representing Chemical Engineering

____________________________

Dean, University Honors College

I understand that my project will become part of the permanent collection of Oregon State University, Honors College. My signature below authorizes release of my project to any reader upon request.

____________________________

Arturo H. Valdivia
# Table of Contents

Chapter 1: Introduction ........................................................................................................ 1

1.1 HfO₂ Devices ........................................................................................................... 2
1.2 Thesis Overview ....................................................................................................... 2

Chapter 2: RRAM Overview .......................................................................................... 4

2.1 Switching mechanism ............................................................................................. 6

Chapter 3: Peer Literature Research ............................................................................. 8

3.1 Electrode Importance ............................................................................................. 8
3.2 Forming Kinetics ..................................................................................................... 9
3.3 Observed Switching Dynamics .............................................................................. 10

Chapter 4: Methods ...................................................................................................... 11

4.1 Bottom Electrode ................................................................................................... 11
4.2 Atomic Layer Deposition of HfO₂ ........................................................................ 11
4.3 Top Electrode ......................................................................................................... 12
4.4 I-V Testing ............................................................................................................. 12

Chapter 5: Results and Discussion .............................................................................. 13

Chapter 6: Conclusion .................................................................................................. 15

6.1 Future Work ........................................................................................................... 15

Bibliography .................................................................................................................. 16
List of Figures

Figure 1: Basic memristor device structure.  
Page 4

Figure 2: Plot on/off cycle produced by HP using a Pt/TiO2/Pt device. Figure adapted from [1]  
Page 5

Figure 3: Diagram representation of the set and reset process of a memristor.  
Page 5

Figure 4: Suggested filament switching mechanism of a memristor.  
Page 6

Figure 5: Waveform of voltage applied to devices. Figure adapted from [7]  
Page 9

Figure 6: Film thickness points taken with ellipsometer.  
Page 12

Figure 7: Plot of Log Absolute Current vs. Voltage showing bipolar switching for a 7854 \( \mu \text{m}^2 \) Al/HfO2/TaN device  
Page 14

Figure 8: Plot of Log Absolute Current vs. Voltage showing bipolar switching for a 1257 \( \mu \text{m}^2 \) Al/HfO2/TaN device  
Page 14
ABSTRACT FOR THE THESIS OF

Arturo Valdivia for the degree of Honors Bachelor of Science in Chemical Engineering presented on June 5, 2013

Title: I-V Characteristics of Al/HfO$_2$/TaN RRAM Devices

The memristor is a resistive switching random access memory (RRAM) with a basic metal/insulator/metal (MIM) structure. These nano devices are nonvolatile, have a conceptually simple crossbar device structure, are power efficient and have the capability of switching between high and low resistance states in nanoseconds making them promising to replace current forms of memory storage. In this thesis Al/HfO$_2$/TaN RRAM devices were synthesized and bipolar switching was observed. I-V curves for devices of different areas were obtained and characteristics with regards to the set and reset voltages were attributed to literature trends for future production of stable devices.

Abstract approved:

John F. Conley Jr.
I-V Characteristics of Al/HfO2/TaN RRAM Devices
Acknowledgements

The Author would like to express sincere gratitude to Dr. Conley for allowing him to complete this work under his guidance. The Author would also like to thank Dr. Herman and Dr. Rochefort for agreeing to participate as committee members. Finally the Author would like to thank his family and friends for their support they have provided him throughout his life.
Chapter 1: Introduction

As the transistor based flash memory approaches physical limitations that will bring an end to Moore’s Law scaling, a replacement technology is being sought to replace the transistor and allow for continued growth in memory capacity. The potential end of our ability to scale flash nonvolatile memory in the next few years has increased interest in the technology known as the memristor. Memristors are nano devices that are nonvolatile, have a conceptually simple crossbar device structure, the capability of switching between high and low resistance states in nanoseconds, and are power efficient. These qualities make the memristor a potential replacement for DRAM, flash, and optical storage.

The memristor is a resistive switching random access memory (RRAM) with a basic metal/insulator/metal (MIM) structure. The insulating material is an oxide thin film, with the most notable being TiO$_2$ after the development of a functioning device by HP [1]. Published device structures include a cross bar array where the oxide film is deposited between perpendicular metal electrodes in an array fashion. A simple device configuration for testing new materials is a dot structure where the oxide film is sandwiched between two metal electrodes.

Despite increased worldwide interest and extensive research since the 2008 publication by HP on the development of a functioning TiO$_2$ based memristor [1], the physics of the switching mechanism is still not well understood. Fundamentally, the mechanism for resistive switching in memristors must be fully understood in order to produce and implement the technology in the
future. Although many models have been investigated, one type of model is that the switching mechanism follows that of a conductive filament model where oxygen vacancies are driven through electrochemical migration to form these conductive paths.

1.1 HfO$_2$ Devices

Memristor behavior has been attributed to numerous materials such as ZTO [2], TiO$_2$ [1], IGZO [3] and HfO$_2$ [4], all of which show varying performance and reliability. In order to reproduce robust devices of varying semiconductor materials that exhibit high endurance capability necessary for RRAM production, research devices are required to produce pools of data that would allow proper characterization between materials. The process of characterization requires that a single device be capable of outputting the necessary data, in the case of memristors, generation of on/off cycles on the order of at least $10^2$ is desirable. HfO$_2$ has shown excellent performance and reliability in previously published research, generating cycles greater than $10^{10}$ [5]. Due to its proven robustness and superior reliability HfO$_2$ [4], was chosen as the material for this thesis.

1.2 Thesis Overview

This thesis will provide the following information in the order that is presented in this brief summary. First, the introduction of RRAM concepts such as device structure, bi-polar cycle characteristics, RRAM terminology and switching mechanism that have been proposed in peer literature. Second, information from review literature pertaining to top and bottom electrode materials, forming kinetics along with switching dynamic pertaining to HfO$_2$ will be presented to obtain higher device characterization concepts. Third, the methods used to develop working
memristor devices and the characterization techniques used in this thesis are described in detail. Fourth, the results that were obtained from the devices are discussed. Finally, a summary of the research is presented along with recommendation for continued work.
Chapter 2: RRAM Overview

RRAM is a form of non-volatile memory that utilizes voltage or current induced changes in the conductance of the insulating dielectric material. A typical structure of a memristor device is presented in Fig. 1. The structure consist of a metal bottom electrode (BE) followed by a dielectric material which is then capped by a metal top electrode (TE).

![Figure 1. Basic memristor device structure.](image)

The resistance of the insulating material is then capable of being varied as voltage is applied to either terminal. RRAM is programmed based on the state of the device, as voltage is increased the current through the dielectric material increases until a step increase or decrease of several orders of magnitudes in current is experienced. The device switching from a high resistance state (HRS) to a low resistance state (LRS) is referred to as the set process and the device is said to be on. Applying the reverse polarity of voltage from the set process switches the device back to the high resistance state and is referred to as the reset process and the
device is then in the off state. Devices that change state with opposite polarity for set and reset are said to bipolar. Conversely devices that change state with a single voltage polarity are classified as unipolar. The focus of this thesis is on the behavior of bipolar devices. A characteristic voltage vs. current plot that was presented by HP for their Pt/TiO$_2$/Pt device is depicted in Fig. 2 [1] and shows the capability of memristor devices achieving different resistance states.

![Plot on/off cycle produce by HP using a Pt/TiO$_2$/Pt device. Figure adapted from [1]](image)

The set and reset cycle is further represented pictorially in Fig. 3.

![Diagram representation of the set and reset process of a memristor.](image)
2.1 Switching mechanism

The switching mechanism of the memristor is still under scientific debate, although, the majority consensus is that the driving force behind the switching behavior is the formation of filaments due to the electrochemical migration of oxygen vacancies [9]. As a broad overview, this concept is depicted in Fig. 4.

As a voltage is applied to an electrode, the oxygen vacancies will migrate in the direction of the electric field. This process is continued until a conductive filament is formed between the two electrodes and the device reaches the LRS. The filament is then broken by reversing the bias polarity causing the oxygen vacancies to migrate back into the insulating material and revert back into the HRS. Problematically, these devices can form multiple filament paths which can vary the set and reset voltages, two parameters that are necessary for programmable RRAM devices. Furthermore, the number of set/reset cycles a device can undergo, referred to

![Figure 4. Suggested filament switching mechanism of a memristor.](image-url)
as endurance, is directly impacted by the number of filaments formed. As the number of cycles increases so does the formation of filaments. This occurs until a threshold is reached and the number of filaments formed is too great they can no longer be broken down and the device is permanently in the LRS. Scientific research has provided substantial data supporting this switching mechanism some of which will be discussed in section 3.3 of this thesis.
Chapter 3 Peer Literature Research

As previously stated, the understanding of the kinetics of memristor devices are of most importance if they are to be programmed with a numeric logic and used in an RRAM device. This section is to describe the knowledge base with regards to the variables that affect the switching mechanics of memristors. This thesis focuses on HfO$_2$, for this purpose, information regarding HfO$_2$ switching was sought out and is dominantly reported in this section.

3.1 Electrode Importance

Extensive research has been conducted to determine the importance of the electrode material used in memristor devices. It has been reported that metals used for the TE such as Al, Hf, and Ti with a high enthalpy of formation of oxides ($\Delta H_f^0$) exhibit bipolar switching and metals with low $\Delta H_f^0$ such as Pt and Cu lead to unipolar switching [6]. The TE material has also been found to impact the endurance of the devices as the usage of improper materials leads to degradation due to the formation of bubbles underneath the contact, generally the TE is attributed as a stabilizer in memristor devices. A properly chosen TE can effectively produce devices with a higher cycle output. The growth electrode or BE has been shown to directly affect the forming times of memristor devices. This is attributed to the chemical reactivity of the growth electrode and a subsequent formation of an oxygen vacancy rich interfacial electrode oxide layer [6]. Metals with a higher chemical reactivity are capable of reducing the electroforming time due to the readily available oxygen vacancies at the bottom interface that accelerate filament percolation.
3.2 Forming Kinetics

High interest is paid towards the forming kinetics of a memristor device. Area scaling of a device has been shown to be inversely proportional to the forming time, while the forming time was seen to be directly proportional to the applied voltage [7]. Device areas ranging from 0.125-2.544μm² consisting of a HfO₂ dielectric film TiN bottom electrode and Al top electrode were tested to obtain a forming time (τᵢ). The results showed that as the device area was increased, τᵢ reached a saturation time past a critical area. Conversely, as the device area was scaled down τᵢ significantly increased requiring a larger bias to be applied to achieve forming. Studies were also conducted to determine the effect of the testing method by varying the waveform of the applied voltage to determine the effect on τᵢ. Testing methods included altering the waveform of the bias so that long duration pulses at a constant voltage, long duration sweeps and a series of short pulse steps were applied to different devices with the same compliance current (cc). The configuration of this waveform test method is shown in Fig.5.

Figure 5. Waveform of voltage applied to devices. Figure adapted from [7]

The results were quantified by stating a failure time τfailure. This time was designated at the point where the resistance associated with the SET process experienced a 10X increase resulting in a drop in the LRS current and the device is said to be no longer reliable. From the
waveforms above W1, and W2 experienced a wider distributions of increase in resistance in the set process while W3 was more uniform despite having a higher median resistance value than W1 and W2. W3 also experienced the shortest device lifetime but once again had a tighter distribution than W1 and W2. From these results it is theorized that the short pulse periods are able to develop more uniform filaments, a desired quality in a memristor device.

3.3 Observed Switching Dynamics

The switching dynamics of $V_{\text{set}}$ and $V_{\text{reset}}$ in a memristor appear to follow different transient characteristics. Due to the different transient stage, the $V_{\text{set}}$ is seen to have a wide distribution when compared to the $V_{\text{reset}}$. This is attributed to a $\tau_{\text{wait}}$ period where the device experiences a low level current followed by a distinct pause period prior to a jump in current. This finite period of time results in the wide distribution seen in the $V_{\text{set}}$ process. The $V_{\text{reset}}$ process has no such transition and the current directly responds to the bias resulting in a tighter $V_{\text{reset}}$ distribution. It has been reported that $\tau_{\text{wait}}$ gradually increase with an increase in pulse space of the bias. This suggests that the dielectric breakdown may be thermally originated [8] meaning the $\tau_{\text{wait}}$ is essentially the period to accumulate enough thermal energy to achieve dielectric breakdown.
Chapter 4 Methods

This section is an overview of the methods used to construct a memristor device followed by the I-V testing methods used to obtain the I-V characteristic curve for the Al/HfO2/TaN device.

4.1 Bottom Electrode

For this thesis the bottom electrode used for the dot structure devices was TaN. TaN was deposited on Si substrate provided by Intel. The substrates used were 1 inch x 1 inch samples. The deposition thickness was estimated to be 25 nm.

4.2 Atomic Layer Deposition of HfO₂

HfO₂ was deposited via atomic layer deposition (ALD) using the recipe provided in Table 1.

Table 1. ALD recipe used to produce HfO₂ film for memristor device

<table>
<thead>
<tr>
<th>Deposition temperature</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Cursor Temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>Purge</td>
<td>90 °C</td>
</tr>
<tr>
<td>Water Pulse</td>
<td>10 sec</td>
</tr>
<tr>
<td>Hafnium Pulse</td>
<td>0.1 sec</td>
</tr>
</tbody>
</table>

A spectroscopic ellipsometer was used to determine the film thickness. A five point method was used to determine the average film thickness. Fig. 6 depicts this measurement method.
4.3 Top Electrode

The top electrode material used in this research was Al. Al was deposited using a Polaron Thermal Evaporator and a shadow mask patterned with a dot structure array. One Al clip was placed into the tungsten boat, the substrate was then loaded into the substrate holder to overlay the shadow mask. The Polaron was then roughed down by mechanical pump and brought under high vacuum by a diffusion pump settling on pressure of $3.5 \times 10^{-3}$ Pa. The Polaron had been previously calibrated to estimate a 250 nm thickness for the deposited Al thickness at this pressure.

4.4 I-V testing

I-V characterization was completed through the use of an Agilent 4155 semiconductor parameter analyzer (SPA). The device was electroformed using a gradual increase in CC method [2]. A negative bias was applied to the TE while the bottom electrode was grounded. The initial forming cc used was 10 nA, a negative sweep was performed until the CC was reached. The CC was then increased to 50 nA and another negative voltage sweep was conducted until the CC was again reached. This process was repeated, doubling the CC for every sweep until 200 nA CC was reached. Once the 200 nA CC was reached one final forming sweep at a cc of 500 nA was
conducted. The CC was then increased to 16 uA, once this CC was reached the device was determined to be in the LRS. A reverse sweep was then conducted from $-V$ to 0. A positive bias was then applied to the device and a voltage sweep was conducted until a drop of several orders of magnitude in current signaling HRS had been reached. The reverse sweep was again applied, this time from $+V$ to 0 completing one cycle. During the positive sweep no compliance current was used to limit the current of the device. This process was applied to memristors with three device areas, $314 \ \mu \text{m}^2$, $1257 \ \mu \text{m}^2$, $7854 \ \mu \text{m}^2$

Chapter 5: Results and Discussion

The data for the $7854 \ \mu \text{m}^2$ Al/HfO2/TaN device was plotted to show the log absolute current vs. voltage and can be seen in Fig. 7. From the data the $V_{\text{set}}$ is seen to vary from $-1.1 \ \text{V}$ to $-1.6 \ \text{V}$ while the $V_{\text{reset}}$ ranged from $0.2 \ \text{V}$ to $1.1 \ \text{V}$. However, the $V_{\text{reset}}$ experienced a large drop after the second cycle decreasing the range from $0.2 \ \text{V}$ to $0.5 \ \text{V}$. Similarly the data for the $1257 \ \mu \text{m}^2$ device was plotted on a log absolute current vs. voltage scale and can be seen in Fig.8. Both devices show similar characteristics with regards to the $V_{\text{reset}}$ of the device. Like the $7854 \ \mu \text{m}^2$ device the $1257 \ \mu \text{m}^2$ device also experienced a drop in $V_{\text{reset}}$ and settles around a value of $0.5 \ \text{V}$. The $V_{\text{set}}$ for the $1257 \ \mu \text{m}^2$ device also experienced a wide $V_{\text{set}}$ distribution like the $7854 \ \mu \text{m}^2$ device, however, a shift was seen and the $V_{\text{set}}$ was seen to center around $-2.5 \ \text{V}$. This shift in required forming voltage can be correlated to section 3.2 of this thesis as a possible explanation where literature research found that the required set voltage was found to be inversely proportional to the area of the device [7].
Figure 7: Plot of log absolute current vs. voltage showing bipolar switching for a 7854 $\mu m^2$ Al/HfO$_2$/TaN device

The wide distribution in $V_{set}$ can also be explained by section 3.3 where literature research on the switching dynamics found that the set voltage depends on the thermal energy required to break through the dielectric material [8]. Because the voltage wave form was not changed between the testing of the two devices it should be expected that the distribution of $V_{set}$ should be roughly same which is seen in both figures.

Figure 8: Plot of log absolute current vs. voltage showing bipolar switching for a 1257 $\mu m^2$ Al/HfO$_2$/TaN device
No device switching was seen in the 314 µm² device. It could be theorized that the set voltage for the 314µm² device would experience a shift further left and place it outside of the -4 V limit placed on the sweep to prevent device breakdown accounting for the 0 cycles achieved with these devices. It should be noted that devices consisting of a HfO₂ film ranging from the 0.125-2.544µm² experienced on/off switching within a 4 V limit in peer reviewed literature however these devices consisted of different device structure and electrodes.

Chapter 6: Conclusion

Resistive switching was produced with Al/HfO₂/TaN device with effective areas of 7854 µm² and 1257 µm². The \( V_{\text{set}} \) and \( V_{\text{reset}} \) for the 7854 µm² were found to vary between -1.1 and -1.6 V while the \( V_{\text{reset}} \) centered on 0.5 V. The \( V_{\text{set}} \) and \( V_{\text{reset}} \) for the 1257 µm² device were found to center around -2.5 V while the \( V_{\text{reset}} \) showed small variance and centered around 0.5 V. Both devices featured trends found in peer review literature most notably set voltage shift due to device area and set voltage variance. More work is needed to verify these trends.

6.1 Future work

The variance of the set voltage should be investigated for thermal dependence. The temperature during the set sweep could be varied utilizing a thermo chuck stand during probing and the variance of \( V_{\text{set}} \) analyzed at different temperatures. Additionally, a separate pulse test method should be utilized where the pulse duration applied to the device is varied. From the above methods the devices should show a decrease in set voltage variance along with a lower required \( V_{\text{set}} \).
Bibliography


