

Resistive Transition Metal Oxide Memory

Wilkie Olin-Ammentorp, Dr. Santosh Kurinec

Abstract—A process is created at the Rochester Institute of Technology Semiconductor & Microsystems Fabrication Laboratory (SMFL) to create crossbar structures. These structures can be created out of a variety of materials via different patterning methods, and can be used to investigate potential memristive behavior of many different materials. Using the crossbar structure, resistive switching of an Al/TiO_x/Al structure is observed.

Index Terms—Crossbar, memristor, transition metal oxides

I. INTRODUCTION

OVER the previous decade, flash memory has made massive gains in storage density and market share. However, due to fundamental scaling limits being reached, a replacement memory device must be found. Resistive random access memory (RRAM) is a leading candidate to replace flash memory as a storage-class memory. RRAM is a broad classification of devices, all of which share the commonality that their information is stored in the resistance of a cell. In its simplest form, a cell is switched into either a high-resistance or low-resistance to store information.

A phenomenon whereby the resistance of transition metal oxides (TMOs) shifts from a high-resistance state to a low-resistance state after applying an electric field has been known for some time. It has been found that the migration of defects through these films creates conductive pathways which change the resistance of the material. Electrical current and electric fields can cause these pathways to shift and reform, which results in a resistance state which can change based on how the film has been biased. This meets the characteristic of a memristive device, which changes its resistance based on how it has been biased previously. [1]

The use of TMOs to create a resistive memory is a concept which has seen great interest over the past decade. These devices are stable, high-endurance, low-latency, and have been demonstrated at sizes under 5 nm. [2][5]

A process has been developed at RIT to create resistive TMO memory structures. In this process, a bottom electrode is patterned by photolithography and either lift-off or etch. The TMO film is deposited by reactive magnetron sputtering and characterized for thickness, refractive index and electrical resistivity. The top electrode is then deposited and also patterned by photolithography and lift-off or etch. The final devices are then electrically tested for memristive behavior.

II. THEORY

Resistance switching has been observed in many different transition metal oxides; TiO₂, HfO₂, ZrO₂, ZnO, Ta₂O₅, NiO,

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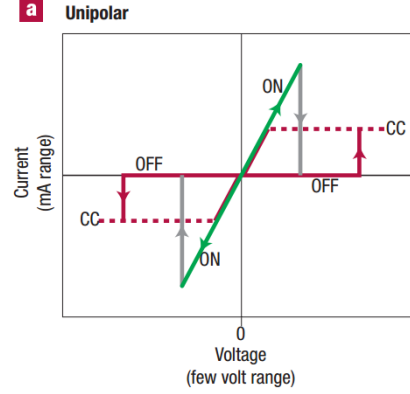


Fig. 1. Current-voltage characteristic of a unipolar RRAM device. [1]

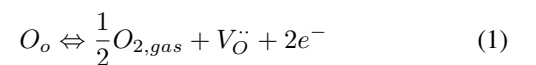
and many others have been used to form RRAM devices. [3][4] In these materials, vacancies or interstitials in the materials' lattices can increase the nearby concentration of free electrons. This increases the local conductivity of the material. As a result, if enough mobile defects can gather to form a pathway of the material's conductive phase, the overall resistance appears to decrease by orders of magnitude.

Several different mechanisms can be responsible for the movement of defects through these materials. Drift, electromigration, Fick diffusion, and thermophoresis (electric fields, electron kinetic energy, concentration gradient, and temperature gradient, respectively) can all influence vacancies to move. [5] These effects can be used on defects with the end goal of changing the resistivity of a material, but their complex interactions makes fully understanding RRAM's mechanisms a challenge.

III. OPERATION OF TiO₂ DEVICES

Titanium dioxide (TiO₂) has been focused on a material for RRAM devices for several reasons: abundance of materials, CMOS compatibility, and good device characteristics. As a result, the resistance switching mechanisms in TiO₂ are better understood than in many other transition metal oxides.

In TiO₂, it is generally agreed that oxygen vacancies are responsible for creating the conductive titanium oxide phase. [3],[5] In a stoichiometric TiO₂ film, an initial electroforming step is required to create the vacancies which will migrate to form conductive channels. The following formula in the Kröger-Vink notation is the reduction-oxidation reaction which drives the creation of vacancies in TiO₂. These vacancies can then arrange to form a conductive pathway. [3]



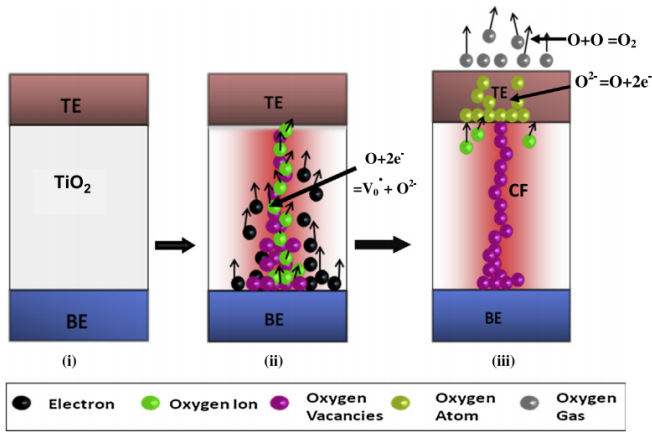


Fig. 2. Illustration of the initial electroforming process in a TiO_2 device. [3]

This reaction drives the formation of vacancies, but also creates gaseous oxygen which can build up and cause damage to the devices by rupturing electrodes. To avoid this, understoichiometric TiO_x films are deposited under a thin stoichiometric layer to create a film which already has defects when deposited, avoiding the need for an electroforming step.

In any case, once a conductive filament is formed, high current levels can cause the filament to dissipate again through Joule heating. This returns the material to a high-resistance state. However, vacancies still exist inside the film. An applied bias can again cause these vacancies to form a conductive filament, returning the material to a low-resistance state. Through the disruption and reformation of these filaments, the material is programmed and deprogrammed, or “set” and “reset.”

However, the filaments responsible for conduction are on the order of 10 nanometers in diameter. As a result, each time the device is set into the low-resistance state, a different filament with a unique resistance and forming voltage may be created. [5] Potential solutions include doping memristive materials to assist pathway formation and reducing device size to the same size as a filament. [3]

IV. RIT CROSSBAR

Only simple structure is needed to investigate the memristive properties of different transition metal oxides. A bottom electrode and top electrode, with the memristive material of interest between them, is sufficient to investigate resistance switching in materials.

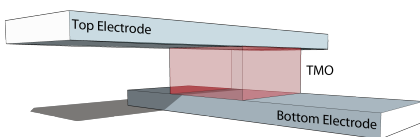


Fig. 3. The crossbar test structure.

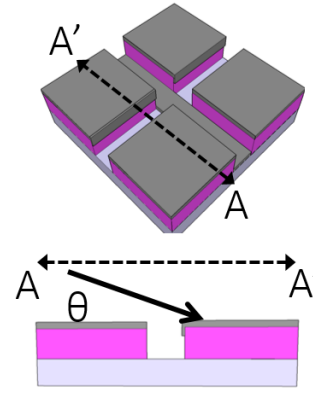


Fig. 4. Illustration of a grazing angle-of-incidence shadow deposition being used to create a self-aligned crossbar. [6]

To fabricate this structure, an investigation into a self-aligned fabrication method for crossbars was begun at RIT in 2013. In this process, a cross structure is patterned into a high aspect-ratio photoresist. The pattern is then loaded into an evaporator at a grazing angle; this causes the resist to form “shadows” in evaporated material. One trough of the cross, aligned towards the source, will have metal deposited. The side of the cross perpendicular to it will be shadowed by the resist, and not be deposited. The memristive film of interest is deposited, and the wafer is then rotated in the evaporator to deposit the top electrode.

While this process appears simple, the wafer must be loaded into the evaporator with a very precise rotational alignment to achieve good results. Due to physical restrictions in the evaporator, the samples had to be loaded very close to the source, which made films non-uniform.

Additionally, the TMO film was deposited uniformly over the entire sample, including the bottom electrodes. This makes good electrical contact difficult unless the film is etched away. As a result, a new process was designed using conventional patterning and lift-off techniques to create the crossbar structure.

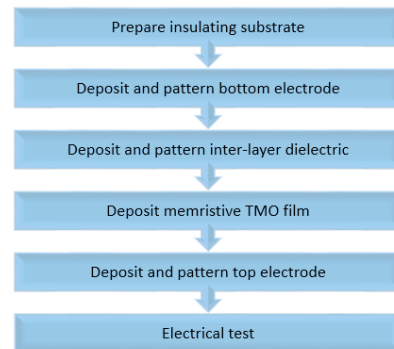


Fig. 5. High-level overview of process flow to create crossbar structures.

In this process, the most important step is the deposition of the memristive film. This determines the characteristics of the resulting devices more than any other, and so the process used must be well-characterized. To accomplish this, a simple

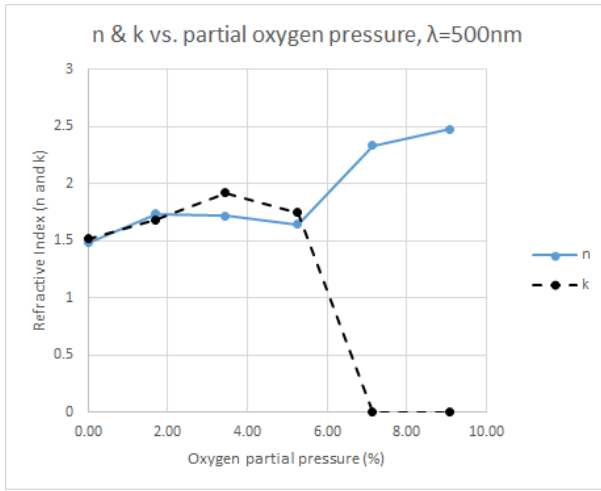


Fig. 6. The resulting refractive indices (at 500 nm) of Ti films sputtered with varying partial pressure of O_2 .

experiment was run to investigate the properties of reactively sputtered titanium oxide films. In this experiment, the partial pressure of oxygen in the sputtering ambient was adjusted from 0% to 9.1%. The resulting films' optical constants, shown in figure 6, were measured by variable-angle spectroscopic ellipsometry. Full experimental conditions are stated in appendix A.

Using sputter conditions obtained from the experiment, a stack of under-stoichiometric and near-stoichiometric TiO_x were reactively sputtered on top of an aluminum bottom electrode. An aluminum top electrode was evaporated on top and lifted off to form the final crossbar structure.

V. ELECTRICAL RESULTS

Initial electrical testing was carried out using a probe station and a parameter analyzer. A voltage sweep while measuring current with no current compliance level showed low levels of current, with one spike in the milliamps range occurring after around one volt of bias had been reached. With no current compliance set, the conductive pathway forms and then is immediately dissipated by high current concentrations causing heating. By setting a compliance level in the hundreds of nanoamps, more controlled set and reset operations were achieved.

As shown in figure 8, both low-resistance and high-resistance states were achieved in this test device. An initial low-voltage bias causes the pathway to form, causing the low-resistance state. The current compliance level and a low voltage keeps the device from resetting into the high-resistance state. When a reset is desired, however, the compliance level can be removed, causing high current levels, heat, and the resulting dissipation of the filament.

Managing the compliance level and the operating voltage of the device in the read state can be a challenge; these settings must be properly managed to keep the device from undergoing undesired sets or resets. As previously mentioned, the non-uniformity of the devices between devices and sequential

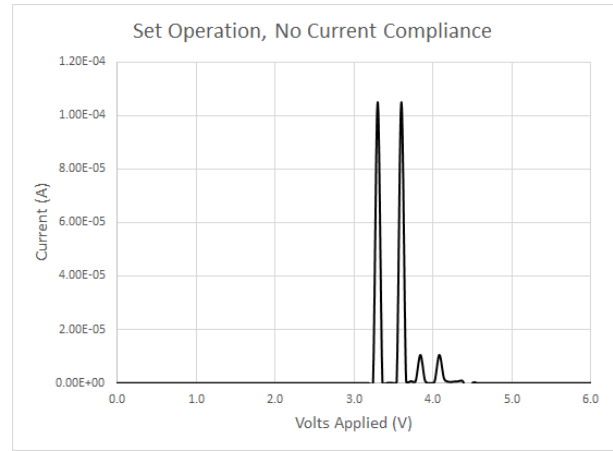


Fig. 7. Electrical results which show sporadic forming and deforming of conductive filaments when no current compliance level is set.

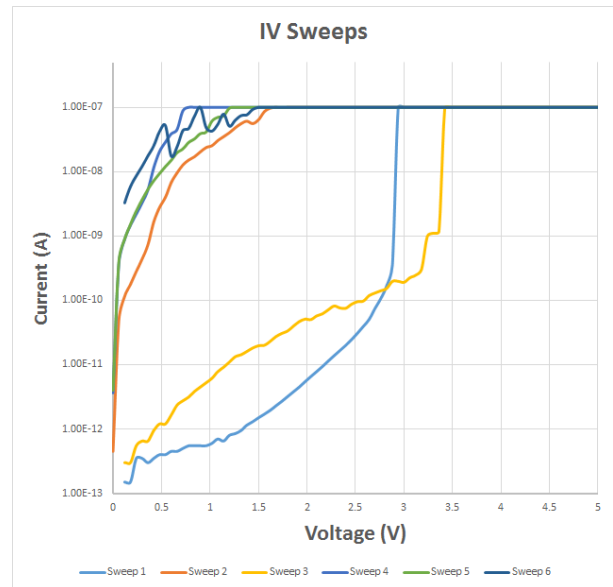


Fig. 8. Current-voltage characteristics from sequential sweeps of a single device. A clear separation between a low-resistance and high-resistance state is seen.

programming and deprogramming in the same device makes operation a challenge.

VI. FUTURE WORK

This work was mainly done to characterize the fabrication process and to enable testing of devices with different films. The effects of doping the memristive film with impurities and further refinement of the sputtering conditions of titanium dioxide and other transition metal oxides will be investigated.

VII. CONCLUSION

To investigate the memristive properties of different transition metal oxide films, a crossbar fabrication process was designed. A brief experiment investigating the properties of reactively sputtered titanium oxide films was carried out. The conditions from this experiment were used to create a memristive film stack which was tested by the crossbar structure.

Electrical results showed memristive behavior, paving the way for future work with different materials.

APPENDIX A CONDITIONS FOR REACTIVE TiO₂ SPUTTER EXPERIMENT

Run	O ₂ partial pressure (mT)	Ar partial pressure (mT)
1	0	12
2	0.2	11.8
3	0.4	11.6
4	0.6	11.4
5	0.8	11.2
6	1	11

The first sputter was preceded by a 300-second pre-sputter to clean the titanium target. Subsequent sputters had a 20-second pre-sputter to reach steady state under the new ambient conditions. All sputters were done at 300 Watts of power applied to a 4 inch target.

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Wilkie Olin-Ammentorp entered the Microelectronic Engineering program at the Rochester Institute of Technology in Fall 2010, and is graduating in Spring 2015 with a BS in Microelectronic Engineering and an MS in Materials Science.