Study of Resistive Switching in Titanium Dioxide (TiO₂) Thin Film for the Application of Non-Volatile Memory: A Review

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Abstract: Resistive switching devices have now become important candidates for non-volatile data memories often referred to as Resistive Random Access Memories (RRAM) or Memristors. Resistive switching is a physical phenomenon where a dielectric suddenly changes its resistance under the action of strong electric field. The change in resistance is non-volatile so used in resistive random access memories which are a promising candidate for data storage applications. These devices were mainly fabricated by means of top down approach but because of the size limits, bottom up approach is used. This paper discusses and focuses on the study of resistive switching in Titanium Dioxide (TiO₂) thin film for use in non-volatile memories.

Keywords: Resistive Switching, thin film, TiO₂, memristor.

I. INTRODUCTION

The demand for digital non-volatile memories is increasing with increase in data. Also the physical limitations are predicted to restrain the miniaturization of an IC. So there is a need of non-volatile memories which overcomes the limitations of miniaturization also. Resistive random access memories are the promising devices for use as non-volatile memories. Their operation is based on resistance switching - a physical phenomenon where resistance gets switched from one state to other in presence of electric field. The basic structure of a RRAM device is capacitor like where there are metal electrodes and a dielectric in-between. So RRAM is three layered where the insulator/ semiconductor thin film is sandwiched between two metal electrodes thin films. The insulator/ semiconductor layer is the functional layer of the device and is made of transition metal oxide. The device thus fabricated is excited by electric fields and shows a reversible and repeatable resistive switching [1]. Many top-down techniques like lithography are used to structure the thin-film but alternatively bottom-up techniques like chemical synthesis of nano-particles and their assembly allows the fabrication that overcomes the physical limitations of top-down approaches.

Silicon-based memories like flash memories, dynamic RAM and hard disk drives dominated the market with their set of advantages and disadvantages. Novel memory technologies have been proposed to overcome various problems of silicon-based memories like low write–erase speeds, non-volatility and slow response to magnetic field.

To overcome the disadvantages four random access memories (RAMs) have been proposed: ferroelectric RAMs (FRAMs), magnetic RAMs (MRAMs), phase-change RAMs (PRAMs), and resistive RAMs (RRAMs). FRAMs and MRAMs also have the miniaturization problem because of their large memory cell size. PRAMs require high power for the phase transition between the amorphous and crystalline phases. RRAMs are the promising candidates for the next-generation memories. The size can be scaled down to below 10 nm and their response time can reach nanoseconds (ns) [2]. One more advantage of RRAM is its possible integration into high density matrix type memory using the crossbar architecture where the select transistor can be replaced by a diode. Resistance switching random access memory (RRAM) is a novel memory technology that utilizes switchable resistance states of some materials. These materials act as functional components of the RRAM. Given below is the basic structure of RRAM.

Fig 1: Basic structure and schematic diagram of RRAM in metal-insulator-metal structure and its biasing [3].
Binary metal oxides, transition metal oxides, ternary perovskites such as SrTiO$_3$ and SrZrO$_3$ and even more complex multi-component compounds including the colossal magnetoresistive manganites LaCaMnO$_3$ and Pr$_{1-x}$La$_x$CaMnO$_3$ and cuprate superconductors YBCO and BSCCO are reported to show resistive switching [4].

A functional layer of Fe$_3$O$_4$ nano-particle assembly was one of the first works reported to show resistive switching given by Kim et al. in 2009 [5]. Following this, many iron oxide-based NPs were further investigated for resistive switching e.g., Fe$_2$O$_3$ NP assemblies [6-8]. Resistive switching was also reported for CdS nanoparticles [9], CeO$_2$ nanocubes [10,11], BaTiO$_3$ nanoparticles [12], ZnO nanoparticles [13], NiO NPs [14], Ge–GeO$_x$ nanowires (NWs) [15], and for In$_2$O$_3$ nanorods [16]. Goren et al. demonstrated the resistive switching of assemblies consisting of spherical 3 nm TiO$_2$ nanoparticles in a Co–TiO$_x$ NPs–Co structure [17]. Sol–gel route was used to synthesize the nanoparticles (amorphous). A 55 nm thin film was prepared by spin-coating and the bipolar resistive switching was observed. Table 1 gives a list of binary metal oxide showing resistive switching and their RRAM device characteristics. In this paper resistive switching in Titanium Dioxide (TiO$_2$) for use in non-volatile memories is reviewed.

Table 1: A Representative list of Binary Metal Oxide RRAM device characteristics. Data Are Collected From [24-34].

| Material | NiO | Cu$_2$O | Ti–NiO | TaO$_x$ | Ti/HfO$_x$ | Ti/HfO$_x$ | WO$_x$ | ZrO$_2$/HfO$_2$ | Al:SnO | TaO$_x$/SnO | Hf/HfO$_2$ |
|----------|-----|---------|--------|---------|-----------|-----------|-------|-----------------|--------|------------|-----------|
| switching type | unipolar | bipolar | unipolar | bipolar | bipolar | bipolar | bipolar | bipolar | bipolar | bipolar |
| structure | 1T–1R | 1T–1R | 1T–1R | 1T–1R | 1T–1R | 1T–1R | 1T–1R | 1R | 1T–1R | 1R |
| cell area (μm$^2$) | ~0.2 | ~0.5 | ~0.49 | ~0.25 | ~0.1 | 0.0009 | 0.0006 | 0.0025 | ~1 | ~9000 | 0.0001 |
| speed | ~5 μs | ~50 ns | ~5 ns | ~10 ns | ~5 ns | ~0.3 ns | ~50 ns | ~40 ns | ~10 ns | ~10 ns |
| peak voltage | <3 V | <3 V | <3 V | <2 V | <1.5 V | <2.5 V | <3 V | <2 V | <2 V | <2.5 V |
| peak current | ~2 mA | ~45 μA | ~100 μA | ~170 μA | ~25 μA | ~200 μA | ~1 mA | ~50 μA | ~50 nA | ~30 μA |
| HRS/LRS ratio | >10 | >10 | >90 | >10 | >100 | >100 | >10 | >10 | >10 | >10 |
| endurance | 10$^6$ | 600 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| retention | 300 h@150 °C | 300 h@150 °C | 1000 h@150 °C | 3000 h@150 °C | 10 h@200 °C | 28 h@150 °C | 28 h@125 °C | 3 h@125 °C | 3 h@250 °C |

A. Conduction Mechanisms

The conduction mechanism in the RRAM device is dependent on a resistive switch. Conduction mechanisms are studied upon the analysis of the temperature and voltage dependences of the current in the device. The switching effect takes place inside the insulator and consists in the formation and rupture of conductive filaments between the top and the bottom contacts. As a result, the I-V characteristic is a nonlinear curve known as pinched hysteresis. Initially, the device is normally in the so called OFF state or high resistance state (HRS), characterized by the native oxide resistance $R_{OFF}$, usually very high. If a proper SET voltage $V_{SET}$ is applied to the metal contacts, an abrupt change in the resistance occurs. The device is then switched to the ON state, or low resistance state (LRS), where it shows a lower resistance $R_{ON}$. Decreasing the applied voltage does not immediately restore the OFF state. In fact, a RESET voltage $V_{RESET}$ has to be reached to ensure the transition from the LRS to the HRS. A list of some conduction mechanisms that are used in the analysis of conduction in RRAMs is given in table 2. The conduction mechanism depends on the charge transport through the active materials used in the functional layer and the junction between the electrodes and active materials of RRAMs.
II. RESISTIVE SWITCHING IN TIO$_2$

Titanium Oxide (TiO$_x$) is being investigated for the RRAM application for a long time now. The investigations were focused on the switching mechanism so the knowledge regarding endurance and retention is very little. TiO$_2$ nanomaterial-based memory has been studied due to its ease of fabrication. Titanium dioxide being a binary transition metal oxides, its higher reversible capacity, better structural stability, electronic conductivity and high dielectric constant i.e., breakdown more easily when subjected to intense electric fields is a desirable feature for dense electronic integration. Its nanoparticles are used since its RS properties are observed in single crystals as well as thin films. The compatibility of TiO$_2$ in CMOS, its ability to show unipolar where a single bias polarity is used to switch the sample between the high and low resistance states, as well as bipolar resistive switching (BRS), where both bias polarities are necessary to induce the switching as well as bipolar resistive switching and the abundance of Titanium on the earth’s crust which ensure its economic viability are other reasons TiO$_2$ is used nowadays. In this section, both the unipolar (thermochemical) as well as bipolar (electronic) switching are reviewed. Figure 2 shows unipolar and bipolar resistive switching curves measured in electroformed Pt/TiO$_2$/Pt structure [18].

A. Unipolar Resistive Switching

In unipolar resistive switching, thermochemical redox reactions in TiO$_2$ take place leading to the formation and rupture of local conductive paths called conducting filaments. The Joule heating by the flowing current provides the energy needed for the thermochemical redox reactions. The nature of conducting filaments was far from being clarified. However, the recent advances in experimental techniques have elucidated the essence of conducting filaments. In TiO$_2$, nucleation and growth processes are responsible for conducting filament formation. Conducting filament grows parallel to the direction of electric field. Due to the oxidation of oxygen ions, positively charged oxygen vacancies are most likely generated at the anodic interface in a TiO$_2$-based resistive switching cell and drift and diffuse to the cathode interface by the applied voltage. The electrons are injected at the Schottky barrier in the Pt/TiO$_2$/Pt locally at the cathodic interface. Figure 3 shows the filament nucleation and growth process in detail.

Table 2: Conduction Mechanisms in RRAM

| Conduction mechanisms                  | Characteristic behavior                                      | Temperature dependence | Voltage dependence |
|----------------------------------------|-------------------------------------------------------------|------------------------|--------------------|
| Direct tunneling                        | $J \sim V \exp \left( -\frac{2d}{h} \sqrt{2m^* \phi} \right)$ | None                   | $J \sim V$         |
| Fowler–Nordheim tunneling              | $J \sim V^3 \exp \left( \frac{-4dDqV^2}{3q_{fr}V} \right)$   | None                   | $\ln \left( \frac{J}{V^2} \right) \sim \frac{1}{V}$ |
| Poole–Frenkel emission                 | $J \sim V \exp \left( -\frac{q\phi}{k_B T} \left( \frac{qV}{\pi \varepsilon d} \right) \right)$ | $\ln \left( \frac{J}{V^2} \right) \sim \frac{1}{T}$ | $\ln \left( \frac{J}{V^2} \right) \sim V^{2/3}$ |
| Space charge limited current           | $J \sim \frac{V^2}{d^2}$                                   | None                   | $J \sim V^2$       |
| Hopping conduction                     | $J \sim V \exp \left( \frac{\phi}{k_B T} \right)$          | $\ln \left( \frac{J}{V^2} \right) \sim \frac{1}{T}$ | $J \sim V$         |
| Thermionic emission                    | $J \sim T^2 \exp \left( -\frac{\phi - q\frac{qV}{4\pi \varepsilon d}}{k_B T} \right)$ | $\ln \left( \frac{J}{T^2} \right) \sim \frac{1}{T}$ | $\ln \left( J \right) \sim V^{2/3}$ |

Where, $h$ is the Plancks constant, $m^*$ is effective mass of carrier, $q$ is elementary charge, $k_B$ is Boltzmann constant, $\varepsilon$ is the dielectric constant, $\phi$ is barrier height, $d$ is barrier width.
Fig 2: Typical (a) unipolar and (b) bipolar RS switching curves measured in electroformed Pt/TiO$_2$/Pt structure [18]

Fig 3: The schematic illustration of unipolar RS of TiO$_2$ (a) by increasing the applied bias, the conducting filament begin growing from the cathode (electron injection electrode). (b) Once one of filament touches the anode, the MIM system switches to the “on” state which is called “forming.” (c) By the reset process, the filament rupturing occurred at the anode interface by re-oxidation of conducting filament. (d) By the subsequent set process, the conducting filament is rejuvenated [19].

The filaments formed during SET process are ruptured in the reset process and the ruptured filament can be rejuvenated by the set process. The reset operation is achieved by melting the conducting filaments with sufficient electric current and subsequent cooling down. During the cooling step, the melted material may crystallize into either anatase or rutile depending on the phase of the neighboring TiO$_{2-x}$ material. An amorphous phase is also possible due to sudden and extreme cooling.

B. Bipolar Resistive Switching

Electronic or bipolar resistive switching correlates to a case where the trap-mediated hysteretic electronic conduction is asymmetric with respect to the bias polarity [20]. This stage is reached after the rupture of a conducting filament by the thermochemical reset process. The switching in TiO$_2$ can be divided into the filament ruptured region and the filament region. The filament region, which is composed of the Magnéli phase, can be regarded as an electrode forming an Ohmic contact. The position of the switching layer and the density of traps might be arbitrarily controlled electrically by tuning the filament shape in this electronic switching scheme, and following filament rupture process [21]. As a result, various bipolar switching configurations can be achieved within the Pt/TiO$_2$/Pt structure. This provides a novel method of deriving the switching polarity of memristors electrically, which suggests a new path for the application of ReRAM. Interestingly, the bipolar switching mediated by the ionic migration of oxygen vacancies as well as the trap-mediated electronic bipolar resistive switching occurs in unipolar reset TiO$_2$ sample also. Figure 4 shows various bipolar switching configurations depending on the various electroforming process achieved within the Pt/TiO$_2$/Pt structure.
The actual reason behind the switching is yet to be clarified; apparently it is because of the oxygen vacancy concentration at the switching region since each switching mechanism works in totally different conditions. Figure 5 given below demonstrates the possible states (initial, forming, set, and reset) of resistive switching process. The bipolar resistive switching in TiO$_2$ is caused by the localized drift of oxygen vacancies, which is not the case with other material systems where the main cause is homogeneous migration of oxygen vacancies over interfacial area [22]. Figure 5 shows the schematics of the switching states in un-doped and doped TiO$_2$ thin-film sandwiched between titanium nitride and platinum electrodes [23]. In the cited literature, effect of electric field on bipolar resistive switching through interface control in a Pt/TiO$_2$/TiN structure is investigated.

![Schematic diagram of the possible states (initial, forming, set, and reset) of resistive switching process for the (a) TiO$_2$/TiN and (b) TiO$_{2-x}$/TiN cases. Considering the combined interface effects, the strong or weak Schottky contact and high or low resistive ohmic contact are remarkable. The TiO$_2$/TiN case has no initial vacancy, large oxygen vacancy supply, attraction with excessive vacancy participation, and repulsion with residual vacancy, while TiO$_{2-x}$/TiN case has initial vacancy, small oxygen vacancy supply, attraction with low vacancy participation, and repulsion without residual vacancy. The amount of vacancy participation could be the origin of the different rectifying characters [23].](image-url)
Electroforming-free bipolar resistive switching behavior was reported in TiO$_2$ nanowire networks which were grown on Titanium foil via hydrothermal process [35]. The titanium foil also served as supplier of Ti atoms for TiO$_2$. The TiO$_2$ thin film was sandwiched between aluminium and the titanium electrodes. The device (Al/TiO$_2$ nanowire /Ti) thus fabricated showed reproducible and stable electrical performance with a high OFF/ON ratio that lasted for up to $10^4$ s. It was observed that large density of oxygen vacancies at the Ti/TiO$_2$ interface was generated and that was reported to be the reason for forming free switching.

Resistive switching characteristics of TiO$_2$ nano-rod system were investigated [36]. The TiO$_2$ nano-rods were synthesized by hydrothermal method on FTO substrate which also acted as a bottom electrode. Approximately 700nm was the length of nano-rods and were deposited by the rf-magnetron sputtering at room temperature. The IV characteristics of TiO$_2$ nano-rod arrays in figure 7 was plotted to subdue the leakage current to less than $10^{-4}$ Acm$^{-2}$. The self-selecting resistive switching with nonlinearity up to ~10 for crossbar memory arrays application was studied and discussed which paves way for use in practical crossbar arrays without an additional device steak. The self-selecting resistive switching in single material provides novel ways to overcome the sneak path issue for RRAM in the crossbar arrays structure.
III. CONCLUSION

In this review paper, because of the interesting and promising electrical properties of TiO$_2$ thin films as a high-k dielectric, higher reversible capacity, better structural stability, and electronic conductivity, its RRAM application is studied. TiO$_2$ requires an initial electroforming step, due to which defects are generated in the material and resistance switching proceeds which is a useful and the basic feature for use in non-volatile memory. Material’s functionality and performance are important aspects which are to be studied for mass-production compatible memory and so is an easy and economical fabrication process. So, TiO$_2$ or TiO$_2$ based materials might be used in future for memristor devices. There are still issues and limitations which need to be overcome for use in day to day life, e.g: reliability of the dielectric and resistance switching performances. To overcome the issues, research efforts and developments are going on all over the world, which will help solving the problems and make TiO$_2$ based solid state memory devices of the future.

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