Resistive Switching phenomenon in graphene oxide doped with copper devices

Marina Sparvoli
Centro de Matemática, Computação e Cognição
Universidade Federal do ABC
Santo André, Brasil
marinsparvoli@yahoo.com.br

Mario Gazziro
Centro de Matemática, Computação e Cognição
Universidade Federal do ABC
Santo André, Brasil

***Abstract*—Non-volatile memory technology is significant in the market of electronics products. Until now, Flash memory has dominated the market of non-volatile memories, but due to its scalability problem, scientists have also been calling for new devices. Resistive random access memory ReRAM has attracted great attention due to its potential for flash memory replacement in next generation nonvolatile memory applications. This device is based on resistive switching (RS) phenomenon for operation, which is reversible and can be reversed repeatedly. In this work, device fabrication used doped graphene oxide with copper (GO + 1% Cu) and copper oxide (CuO) thin films. ITO (Indium Tin Oxide) and aluminum were used as contacts. Thin films are obtained by the dip coating technique. The mechanism of the resistive switching effect in doped graphene oxide thin film based devices has been investigated by macroscopic current-voltage (IxV) measurements. The RS originates from the formation and rupture of conducting filaments. In addition, switching effect in these study devices has a clear dependence on the electrode material. ReRAM device structures show unipolar resistive switching behavior.**

Keywords—ReRAM, Resistive Switching, graphene oxide.

I. INTRODUCTION

Electronic memory devices have a lot of applications in almost every area of modern life. Essentially, all modern electronic devices have flash memories in their structures, either embedded or externally attached. The rise of portable electronic devices such as mobile phones, MP3, digital cameras, and netbooks over the past 20 years has led to rampant demand for better technology for non-volatile flash memory (which retain information after removing the power supply) due to its small size cells and low power consumption. However, the scaling of flash memory below 15 nm technology is highly problematic because of the cell structure fundamental limit [1-5].

Resistive random access memories (ReRAM) are a class of emerging devices of non-volatile memories. ReRAM is completely compatible with current CMOS technology, which indicates that it is not necessary a great investment for new processes and these devices have simple capacitor structure with two terminals, which is easy to be integrated to VLSI circuits. Many researchers have expended great effort to understand and develop these new memories by presenting simple metal-insulator-metal structure (MIM), easy to read and write, high storage density and low power consumption. Resistive switching (RS) is the basic phenomenon for the functioning of these memories, in which when a given voltage is applied to the MIM device, it may suffer the switching from initial insulating resistance state (HRS - High Resistance State) to a conductor resistance state (LRS - Low resistance state) [1,2]. The RS has been observed in various materials such as TiO_2, ZnO and AlN, in which two typical behaviors were observed: unipolar switching, which means the resistive switching depends on the amplitude of the applied voltage but not on the polarity; and bipolar switching, which means the resistive switching relies on the polarity of the applied voltage. Unipolar RS shows some advantages, such as higher LRS/HRS current ratio and simplicity of peripheral circuits.

Due to the scalability problem, scientists have also been calling for new materials with advanced properties. Graphene oxide (GO) is a versatile material that can be used in electronic components such as processors and memory chips [6-10]. A research team has successfully used the graphene to develop a transparent memory module storage capacity and sufficient strength to be used as ReRAM memory, whose capacity to store information is of at least one hundred thousand seconds in high temperature environments [11].

Generally ReRAM have 3 to 5 layers of different thin films in its structure. In the design for this work, device fabrication used thin films of graphene oxide (GO) doped with copper (GO + 1% Cu) and copper oxide (CuO).

II. EXPERIMENTAL

A. ReRAM fabrication

Copper oxide (CuO) was synthesized using copper (II) acetate as described by Yoo et al. [3]. A colloidal solution of copper acetate in ethanol was used as precursor. 0.3 g copper acetate monohydrate added to 30 mL ethanol suffered sonication for 1 hour. To make CuO thin films, dip coating was used. Deposition is made as follows: thin films are obtained by dip coating technique. The dip coating apparatus basically consists of a clamp which holds the substrate is dipped in a GO water based solution (graphene oxide) which containing the

978-1-5386-2311-4/18/$31.00 c 2018 IEEE

dopant (1% copper) or CuO. For first film layer, the substrate is dipped in the solution for 30 seconds and then dried for 4 minutes (2 minutes for each side of the substrate) under a 150 W halogen lamp. For second layer film, the same process is performed again. And so forth for each additional layer. It was estimated that the optimal dips number is three (~30 nm each layer, measured by scanning electron microscopy). The layers of CuO and GO are interleaved.

Before and after the deposition of thin films, ITO and aluminum contacts were evaporated, respectively. In one ReRAM device, the first layer of ITO (~430 nm) is deposited on a glass substrate in sequence, the layers are deposited CuO / GO + 1% Cu / CuO and finally aluminum circle contacts with 0.5 cm diameter. The other device is ITO/GO + 1% Cu/Al.

B. Device characterization

Current and voltage relation can be measured by tracer IxV model HP 4140b. A curve is generated by varying the voltage. For the device to be considered a ReRAM resistive memory, the graph of the current in a voltage rising curve must have a format different from the curve obtained for the curve in a downward tension. An important memory device mechanism is the transition from the high resistance state (HRS) to the low resistance state (LRS) under applied voltage variation. It may be more useful for the device to have a fast switching response in the critical voltage where the transition occurs HRS to LRS.

III. Results

Two devices were manufactured and analyzed. The difference between them is thin film layers of copper oxide. Both resistive memories had unipolar behavior.

A. ITO/GO+1% Cu/Al ReRAM

Typical current-voltage curve measured at room temperature is shown in Fig. 1.

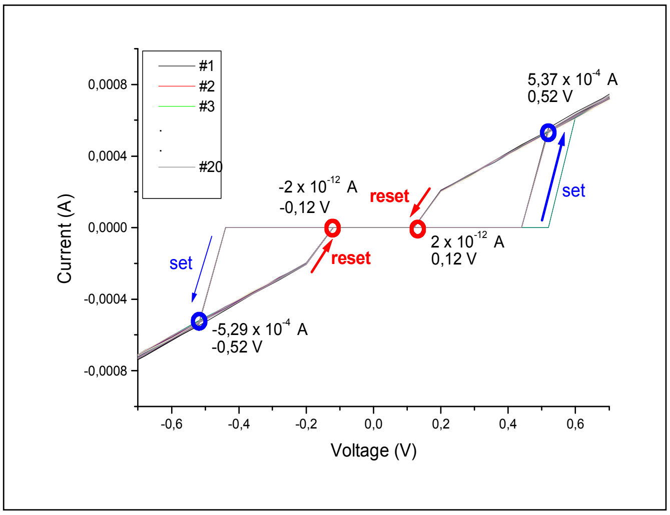

Fig. 1. I-V characteristics of ITO/GO+1%Cu/Al.

Principle of ReRAM is the device able to be abruptly switched between high resistance state (HRS) and low resistance state (LRS) by applying voltage. HRS represents off state while LRS represents on state. Resistive switching could be related to a non-volatile memory effect.

ReRAM device structure shows unipolar resistive switching behavior (Fig. 1), which can be attributed to conductive filament mechanism. Switching mechanism on graphene oxide based devices is usually attributed to formation and rupture of conductive filaments in an insulator.

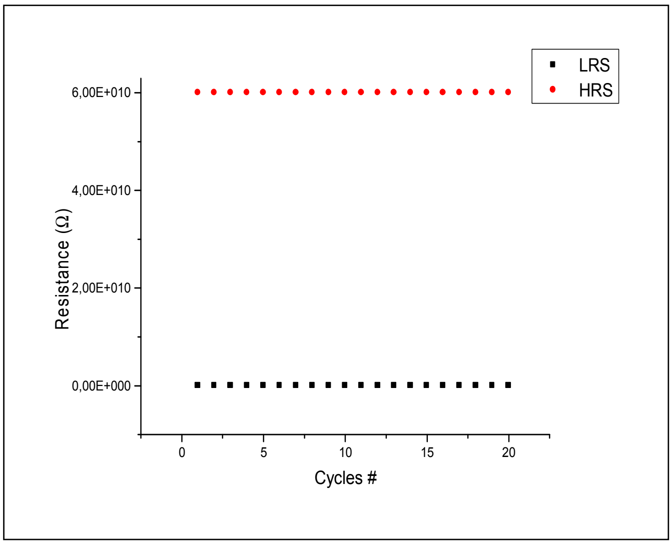

Fig. 2. Initial endurance test for ReRAM structure.

Endurance performance is one of the most important characteristics for applications to non-volatile memory. Fig. 2 shows the endurance results of the ITO/GO+1% Cu/Al.

The 30 nm-thick ReRAM has a LRS of 968 Ω and a HRS of $6x10^{10}$ Ω making it a potential candidate for applications such as non-volatile devices.

B. ITO/CuO/GO+1% Cu/CuO/Al ReRAM

In the measurements of these devices, ReRAM forming results was performed using a HP Model 4140B module.

This memory can be operated in the range of voltage from -2 V to 2 V with compliance current (CC) of 10 mA. According to Fig. 3, unipolar resistive switching from high resistance state to low resistance state (set) occurs under the same bias as LRS to HRS (reset). In Fig. 3 is presented a 20 cycles graph. In this initial study, the purpose is to measure the reproducibility of device behavior.

This device has a different behavior if compared with the other ReRAM: there is an abrupt change in 0.2 V. Probably the addition of copper oxide caused this phenomenon: there was the presence of cations in formation of conductive filament.

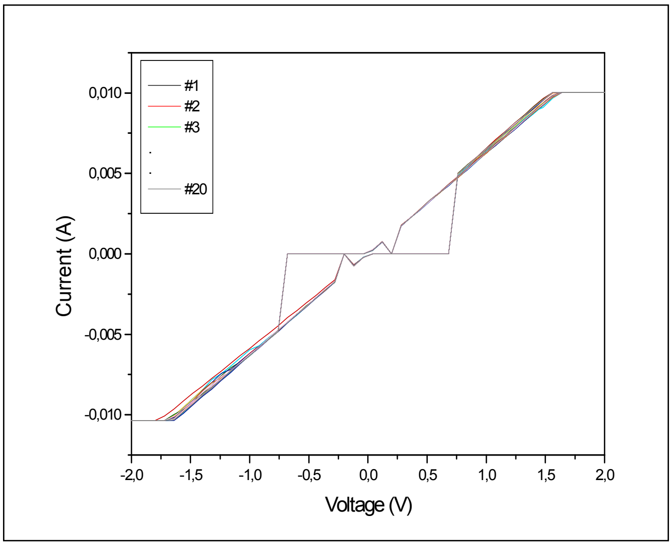

Fig. 3. Cyclic voltammograms.

According to Yoo et al. [3], CuO appears to play an important role in supplying charge carriers.

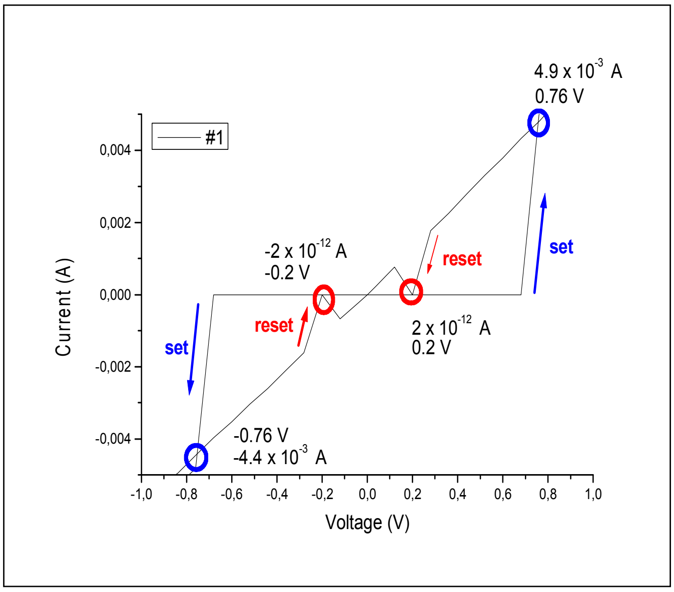

Fig. 4. Typical I-V curves of ITO/CuO/GO+1%Cu/CuO/Al structure.

Current exponentially grows as voltage reaches a certain value. When the filament is established, the device switches into low resistance state (set). In the case of this unipolar device, RS occurs in -0.76 V and 0.76 V (Fig. 4). Metal oxide unipolar filamentary switching is caused by purely thermal oxidation and reduction of the filament.

During the reset process, it is commonly assumed that the conductive filament loses continuity from one electrode to another one, but this affects a small section of the filament. According to Marinella [12], the set operation is forming a conducting pathway of oxygen vacancies and when the abrupt switch between the low resistance state and the high resistance state occurs, the thinnest portion of this filament is dissolved due to Joule heating.

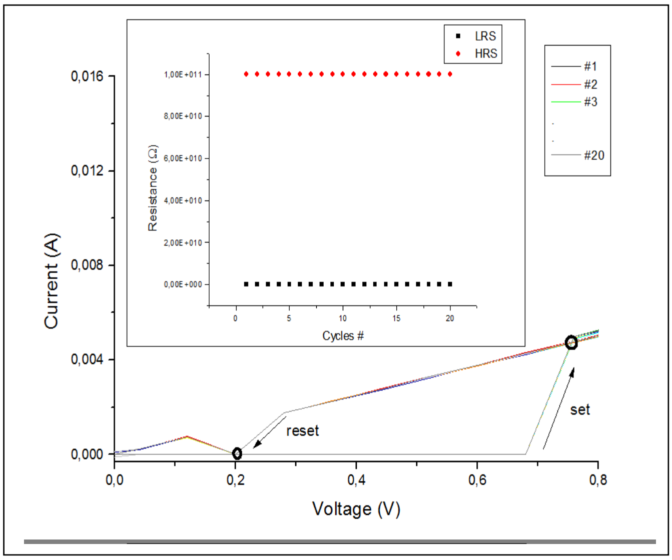

Fig. 5. I-V characteristics of ITO/CuO/GO+1%Cu/CuO/Al. The upper left inset is high resistance state and low resistance state depending on the switching cycle.

Fig. 5 illustrates an endurance test for ITO/CuO/GO+1%Cu/CuO/Al ReRAM structure. Endurance test is similar to endurance tests for memory devices. This device has a LRS of 152 Ω and a HRS of $1x10^{11}$ Ω.

It is important to know the characteristics of the new devices developed, such as voltages where SET and RESET occur, when an application is expected in the future. It is also important to record the voltage range where resistivity changes occur to conclude if the device is optimized for energy consumption. In these unipolar devices it is possible to verify that the formation and destruction of the filament occurs due to the formation of oxygen vacancies present in the graphene oxide. Doping with silver has influence on the behavior of resistive memories, since in the literature it is verified that ReRAMs deposited with pure graphene oxide are bipolar [3]. An interesting point to note is the fact that the material of the insulation layer, the contacts and the combination of layers are factors that give characteristics unique to each device: when layers of copper oxide were added, it was possible to verify thorns in the current versus voltage response curve of the device.

In future research, the intent is to apply these resistive memories in the area of neuromorphic computing. The cells will be miniaturized and arranged in an array architecture (Fig. 6). Algorithms will be created for writing and reading bits in each cell, and from this will be developed a programming for cells operate as neurons.

For the writing operation and with the assistance of a microcontroller, each unit of the matrix will be programmed with specific voltages, those observed in the measurements of the devices (Fig. 1 and Fig. 4), which will allow the formation of the filament between the contacts and due to this fact a high logical level will be written in this ReRAM cell. For the low level, it will also be made use of specific measured voltages that will destroy the filament, thus increasing the resistance between the contacts.

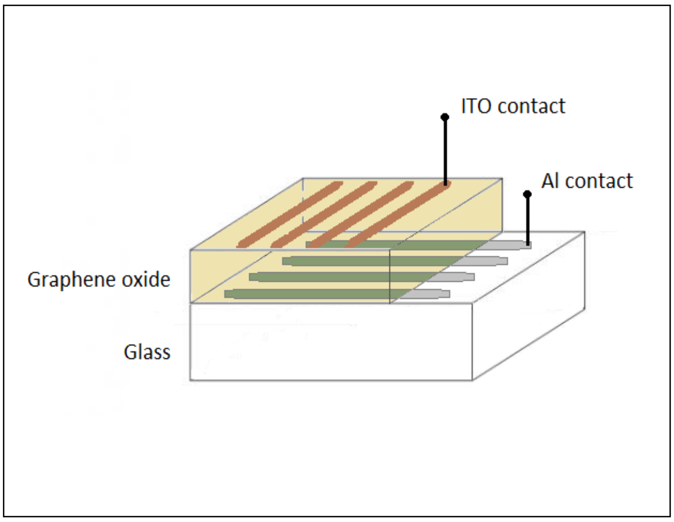

Fig. 6. Resistive random access memories array architecture.

For reading operation, an algorithm will be used that allows the measurement of resistance in the ReRAM unit. The code must interpret the read value; for this purpose a resistance range for high level and another range for low level will be defined.

According Indiveri et al., The idea of linking the type of information processing that takes place in the brain with theories of computer science dates back to the origins of this area [13]. Neuromorphic computing is based on our understanding of brain architecture and its information processing system, as well as its intricate relationships by referring to the complex networks in which the behavior of each individual cell unit affects the behavior of the whole. The neural networks of the brain transmit information in electrical pulses, modulate the synaptic intensities or the value of interconnections based on time and store those changes locally in the interconnections. Intelligent behaviors arise from the cooperative and competitive interactions between the multiple regions of the brain neural networks with the environment. The ReRAMs, in the same way, store the information of the changes in the system with values of resistivity. When these devices are programmed using genetic algorithms, it is possible to make use of the system for application in machine learning.

IV. CONCLUSIONS

In conclusion, we have fabricated rGO-based ReRAM devices by dip-coating. These devices exhibited unipolar RS characteristics. An endurance of 20 cycles for each state was achieved. The presented devices are unipolar. Such behavior is an advantage as it prevents the device from dissipating heat by Joule effect and the change from high resistance state to low resistance state occurs in the same polarity as for the reverse path. In addition, set and reset occur between 0 and 1 V for both devices, which saves energy.

Thinking in terms of obtaining the devices, process and waste disposal, we have an optimization, since the process of obtaining the memories is simple, low cost and there is no generation of toxic or large quantities of waste. If we think about the production of materials, some techniques are expensive (such as MBE or molecular beam epitaxy) and others generate toxic materials (such as the production of silicon oxide that sometimes employs silane gas). Graphene oxide does not pollute and is still derived from carbon, which is abundant. Production process is simple, efficient and inexpensive. It can be made with cheap equipment. Moreover, due to the simplicity, the reproducibility of the devices can be made on a large scale.

ACKNOWLEDGMENT

The authors would like to thanks FAPESP, CNPq and CAPES for financial support.

REFERENCES

[1] A. Siemon, S. Menzel, R. Waser, E. Linn, "A Complementary Resistive Switch-Based Crossbar Array Adder," in Emerging and Selected Topics in Circuits and Systems, IEEE Journal on , vol.5, no.1, pp.64-74, March 2015.

[2] J. S. Lee, S. Lee and T. W. Noh, "Resistive switching phenomena: A review of statistical physics approaches". Applied Physics Reviews, 2, 2015.

[3] D. H. Yoo, T. V. Cuong, S. H. Hahn, "Effect of copper oxide on the resistive switching responses of graphene oxide film", Current Applied Physics, Volume 14, Issue 9, Pages 1301-1303, 2014.

[4] J. Xu et al., "Scaling-down characteristics of nanoscale diamond-like carbon based resistive switching memories", Carbon, Volume 75, pp. 255-261, 2014.

[5] H. Tanaka, K. Kinoshita, M. Yoshihara, S. Kishida, Satoru, "Correlation between filament distribution and resistive switching properties in resistive random access memory consisting of binary transition-metal oxides", AIP Advances, 2012.

[6] G. Katsukis, C. Romero-Nieto, J. Malig, C. Ehli, D. M. Guldi, "Interfacing Nanocarbons with Organic and Inorganic Semiconductors: From Nanocrystals/Quantum Dots to Extended Tetrathiafulvalenes", Langmuir, pp. 11662−11675, 2012.

[7] I. Kaminska, A. Barras, Y. Coffinier, W. Lisowski et al. "Preparation of a Responsive Carbohydrate-Coated Biointerface Based on Graphene/Azido-Terminated Tetrathiafulvalene Nanohybrid Material", Appl. Mater. Interfaces, pp. 5386−5393, 2012.

[8] I. Kaminska, M. R. Das, Y. Coffinier, J. Niedziolka-Jonsson et al. "Preparation of graphene/tetrathiafulvalene nanocomposite switchable surfaces", Chem. Commun., pp. 1221–1223, 2012.

[9] P. A. Denis. "Chemical Reactivity of Electron-Doped and Hole-Doped Graphene". J. Phys. Chem. C, pp. 3895−3902, 2013.

[10] Lu, W; Soukiassian, P.; Boeckl, J."Graphene: fundamentals and functionalities", MRS Bulletin, v.37, 2012.

[11] H. D. Kim et al. "Transparent Multi-Level Resistive Switching Phenomena Observed in ITO/RGO/ITO Memory Cells by the Sol-Gel Dip-Coating Method." Scientific Reports, 2014.

[12] Marinella, M. J. "Emerging Resistive Switching Memory Technologies: Overview and Current Status", IEEE, 2014.

[13] G. Indiveria;B. Linares-Barrancob, R. Legensteinc, G. Deligeorgisd, T. Prodromakise. "Integration of nanoscale memristor synapses in neuromorphic computing architectures", 2013.