Memristor device fabricated from doped graphene oxide

Marina Sparvoli, Mario A. Gazziro, Jonas S. Marma and Gabriel Zucchi

Abstract— **Resistive switching (RS) is the basic phenomenon for the operation of resistive memory ReRAM. A specific electrical voltage is applied in the MIM (metal-insulator-metal) device, it can undergo switching from its initial insulator resistance state (HRS - high resistance state) to a low resistance state (LRS). There is a strong relationship between the materials used in the composition of these devices and their characteristics. In this work, resistive memory based on silver-doped graphene oxide was characterized and its voltage response varying as a function of voltage was obtained. SET and RESET are caused by the redox reactions of graphene oxide layer at the interface between electrodes. Defects as oxygen vacancies in oxide material play a key role for the resistive switching. There is another factor that can influence the operation of this device and threshold switching: silver present in the graphene oxide composition could interfere with the filament formation. In summary, the resistive switching behavior of rGO+0.1%Ag/GO+1%Ag/Al device was investigated, which reveals electric characteristics and SET/RESET voltages. In addition, a threshold switching characteristic is revealed.**

Index Terms— **ReRAM, Resistive Switching, graphene oxide.**

I. INTRODUCTION

ARTIFICIAL neuron is a logical-mathematical structure that seeks to simulate the form, functions and behavior of a living neuron. In this way, the dendrites were replaced by entrances, whose connections with the artificial cell body are carried out by elements called weight (simulating the synapses). The input stimuli are processed by the sum function, and the firing threshold of the biological neuron has been replaced by the transfer function. The basic idea of neuromorphic approaches is to consider resistive memories (ReRAMs) as artificial synapses. According to Indiveri and his team, the idea of using ReRAMs as neural simulations comes from the concept of Crossnets introduced by Likharev, where memories serve as interconnectors that correspond to binary synapses [1].

Resistive memories are passive elements that store information without losing it when the power supply is ceased. They work through a phenomenon called resistive switching, where there is a transition from a high resistance state to low resistance state (SET) and vice versa (RESET) caused by the formation (or disintegration) of a filament in the insulation material between conductive contacts; the structure of this device is usually composed of metal-insulation-metal (MIM) [2]. A specific electrical voltage is applied in the MIM device, it can undergo switching from its initial insulator resistance state (HRS - high resistance state) to a low resistance state (LRS) [3]. There is a strong relationship between the materials used in the composition of these devices and their characteristics.

According Gale, the first commercial suggestion for memristors was memory due the fact memristor's small feature size could offer an increase in memory density, not consuming much energy for its operation and could be used for multi-state memory [4]. Besides, the same technology used for manufacture of CMOS-based memories can be employed in the construction of resistive memories.

Graphene oxide (GO) is a versatile material that can be used in electronic components such as processors and memory chips. GO is not a natural product and results in a non-stoichiometric "molecule". Basically, graphene oxide is defined as a layer of graphene decorated with oxygen functionalities [5]. Graphene is considered to be the basis of the entire family of carbon materials, with the exception of diamond [6-9]. For its production several methods have been researched, exemplified by exfoliation, deposition by the CVD technique, among others [10].

The aim of this study is graphene oxide deposition and its application in a resistive memory contact. Resistive memory based on silver-doped graphene oxide was characterized and its voltage response varying as a function of voltage was obtained.

II. EXPERIMENTAL

A. ReRAM fabrication

Deposition of bottom contact and insulator layer was made as follows: thin films are obtained by dip coating technique.

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M. Sparvoli is with Centro de Matemática, Computação e Cognição, Universidade Federal do ABC, Santo André, Brazil (corresponding author to provide phone: 55-11-3091-9719; fax: 55-11-3091-5664; e-mail: marinsparvoli@yahoo.com.br).

M. Gazziro, Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, Universidade Federal do ABC, Santo André, Brazil (e-mail: mario.gazziro@ufabc.edu.br).

G. Zucchi is with Centro de Matemática, Computação e Cognição, Universidade Federal do ABC, Santo André, Brazil (e-mail: gabriel.zucchi@aluno.ufabc.edu.br).

J. S. Marma is with Centro de Matemática, Computação e Cognição, Universidade Federal do ABC, Santo André, Brazil (e-mail: jonas.marma@gmail.com).

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The dip coating apparatus basically consists of a clamp which holds the substrate is dipped in a GO (graphene oxide) water based solution which containing the dopant (1% or 0.1%).

GO doped with 0.1% silver (rGO+0.1%Ag) bottom contact (~ 55 nm) was deposited via dip coating. In the sequence it was subjected to a reduction process with hydrobromic acid to be functionalized and to become conductive. The use of graphene oxide as a contact is a progress when compared to previous works. Through the measurements, it was possible to check the changes in device electrical characteristics.

Insulating layer of graphene oxide doped with 1% silver (GO+1%Ag), where the resistive switching process occurs, was deposited with an approximate value of 35 nm.

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

Device was manufactured and analyzed. The innovation in this study is the use of reduced graphene oxide as a contact. In memory measurements, ReRAM forming results was performed using a HP Model 4140B module.

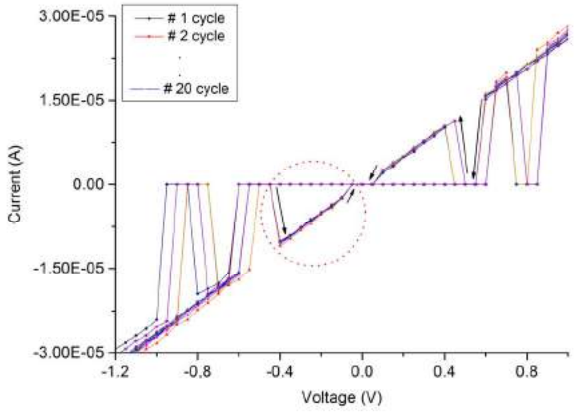

Fig. 1. Typical I-V curves of rGO+0.1%Ag/GO+1%Ag/Al structure.

This memory operates in the range of voltage from -1 V to 1 V. According to Fig. 1, unipolar resistive switching from high resistance state to low resistance state (set) occurs under the same bias as LRS to HRS (RESET). In Fig. 1 is presented a 20 cycles graph. In this initial study, the purpose is to measure the reproducibility of device behavior.

As can be observed, there is an area where measurements have a higher reproducibility, region between -0.45 V and -0.05 V. Therefore it was selected as the target of the analysis from where the filament is formed and destroyed. Formation of the filament between the contacts, which switches the device to the state of low resistivity, occurs due to two processes: ion formation and oxygen vacancies. In the case of this device, the most probable would be the formation of oxygen vacancies due to the fact that GO is rich in oxygen. Such material is formed of graphene sheets connected by this element, and when the necessary voltage is reached, switching is made, forming or destroying the filament between contacts. The instability in the measurements occurs precisely because the contacts are GO and the graphene sheets in this material are not homogeneously distributed.

It is possible to observe that the device presents behavior of unipolar memories, in particular those with threshold switching, or an abrupt transition from the low resistivity state to the high resistivity state (RESET) and vice versa (SET). According to Kim, such memories switch abruptly at the threshold voltage from a highly resistive (off state) to a highly conducting state (on state) and remains in the on state until the applied voltage falls below a minimum voltage (holding voltage), at which point it reverts back to its initial highly resistive state; it is thus symmetric with respect to the polarity of the applied voltage [11].

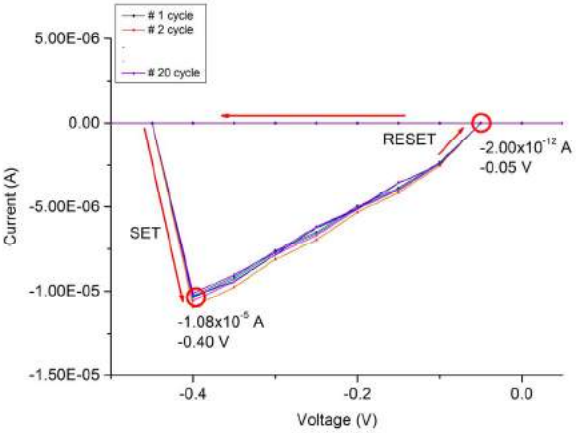

Fig. 2. Detail of the region with reproducible behavior during the 20 measurement cycles.

In the highlighted region, observed in Fig. 2, on state occurs at -0.40 V. When the filament is established, the device switches into low resistance state (SET). Filament formation is explained by the migration of oxygen vacancies from one contact to another. Probably, because bottom contact is formed of rGO and such material has oxygen bonds, there is a migration of vacancies from this contact as well, which would explain the non-reproducibility of current behavior as a function of voltage for certain regions measured during cycles (Figure 1). rGO is formed by graphene sheets interspersed with oxygen, which are not distributed homogeneously. There is the possibility that silver as a dopant is interfering with formation of the filament.

An interesting fact to note is that the type of material used as a contact may have some effect on LRS and HRS values. In literature it is possible to find different results measured for devices with metal contacts. The use of reduced graphene, which, because of its higher resistivity, causes a decrease in the current values of low resistance state [12]. In a previous work, device developed with an ITO (indium tin oxide) bottom contact presented LRS current in order of 10^{-3} A, which means that this variable was 100 times greater than the value presented in this research [14].

It is possible to notice that the use of different materials contacts may result in a change of the magnitude range where there are current values for low resistance state. Metals (aluminum, copper, silver) are used as contact for resistive memories fabrication more commonly [12]. But the case of this device is that the bottom contact is based on reduced graphene oxide. Such material, even doped with silver, presents electrical characteristics close to semiconductors, which would justify a reduction in current values. According to measurements obtained by hall effect, we have that the resistivity of rGO+0.1% Ag has value $4.52\text{x}10^{-2}$ W.cm, conductivity $2.21\text{x}10^{1}$ 1/W.cm and carriers mobility $1.27\text{x}10^{1}$ cm^2/V.s.

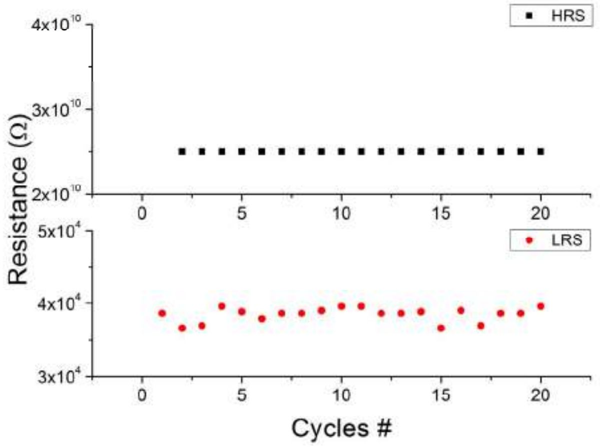

Fig. 3. High resistance state e low resistance state of rGO+0.1%Ag/GO+1%Ag/Al device.

Fig. 3 illustrates an endurance test for rGO+0.1%Ag/GO+1%Ag/Al ReRAM structure. Endurance test is similar to endurance tests for memory devices. This device has a LRS of ~$3.69\text{x}10^4$ W and a HRS of $2.50\text{x}10^{10}$ W.

Figure 1 and Figure 2 show I-V characteristics of graphene oxide memory which describe its analog characteristics suitable for the neuromorphic system. SET and RESET are caused by the redox reactions of graphene oxide layer at the interface between electrodes. Defects as oxygen vacancies in oxide material play a key role for the resistive switching. It is noted that the RESET (HRS to LRS) occurs in values around -0.05 V and SET occurs in -0.40 V, for the same polarity. Being unipolar, there is no influence of the electric current, thus avoiding the joule effect with heating of device. In addition, the SET and RESET occur in a range below -0.50 V, which implies a lower power consumption for it to operate.

There is another factor that can influence the operation of this device and threshold switching: silver present in the graphene oxide composition could interfere with the filament formation. Eventually mobile traps could be formed, destroying the filament fragile section and resulting in abrupt changes of resistance state (Figure 3).

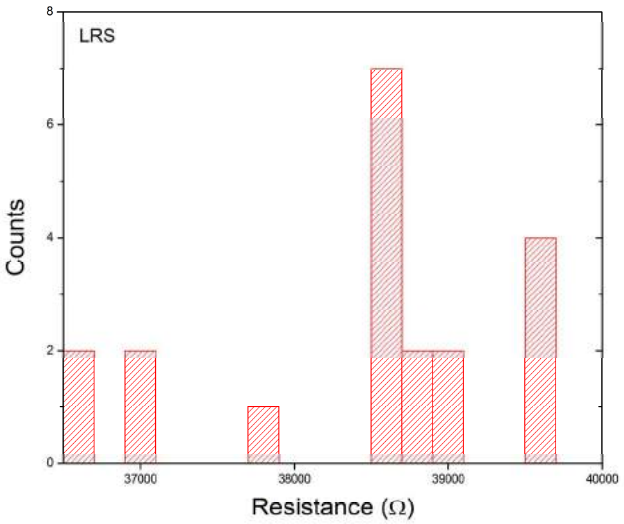

Fig. 4. Low resistance state values count.

In Fig. 4 it can be seen that the resistances vary little for the state where there is a filament formed. Compared with the resistance in the HRS, which is about six orders of magnitude higher, this oscillation in the LRS is insignificant.

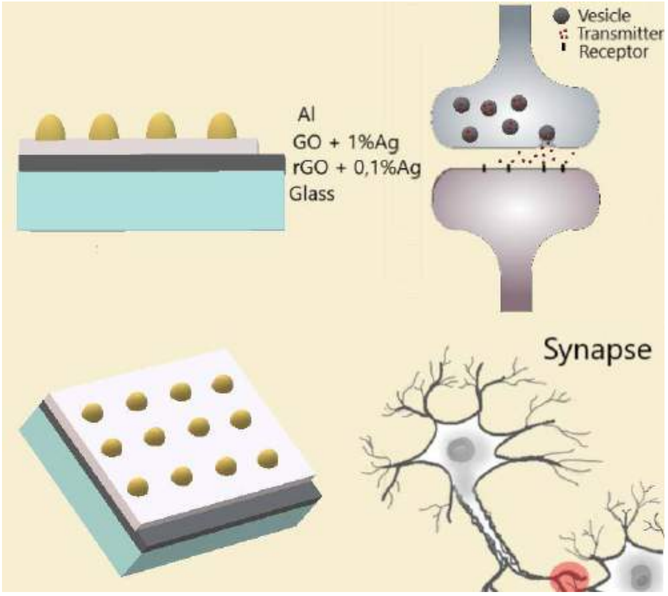

Fig. 5. Comparison of the device with the biological model.

This memory is a memristor which may have several usages in soft computing applications. An example of such application is adaptive networks: the memristor resistance may be used to represent different synaptic weights (Figure 5), and one may build a circuit taking advantage on the modifications easiness of its resistance to produce the necessary weight adjustments. This may be justified by the convenience and potential performance gain by making these processes in specialized machines, built to emulate the biological networks instead of running algorithms in a simulated environment on a Von Neumann based machine, which is intolerant to inaccuracies and centralized, the opposite of biological neural networks.

Sah [13] suggests an example of emulation of such synaptic weights in which the memristors are arranged in a bridge. The circuit that behaves similarly to a Wheatstone bridge, capable of generating a voltage between its top and bottom nodes corresponding to the multiplication of a voltage applied to its input by a weight factor. At sufficient intensities, this voltage applied to the bridge is capable to increase or decrease the weight factor.

IV. CONCLUSIONS

In summary, the resistive switching behavior of rGO+0.01%Ag/GO+1%Ag/Al device was investigated, which reveals electric characteristics and SET/RESET voltages. In addition, a threshold switching characteristic is revealed. We have fabricated rGO-based contact device by dip-coating. This device exhibited unipolar RS characteristics. An endurance of 20 cycles for each state was achieved. Study of electrical variables of this device evidenced that the use of reduced graphene oxide as contact is promising. In addition, it was noted that the use of different materials as bottom contact interferes in the operation of resistive memory.

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Marina Sparvoli was born in São Bernardo do Campo, São Paulo, in 1983. She received the B.S. degree in physics from Universidade de São Paulo, São Paulo, in 2005 and the Ph.D. degree in electrical engineering from Universidade de São Paulo, São Paulo, in 2011.

Since 2012, she has been a Titular Professor with the Departamento de Ciências da Computação e Sistemas de Informação, UNIP (Universidade Paulista). In 2013 she bacame Professor of Universidade Federal do ABC.