frontiers in Materials

MINI REVIEW
published: 31 January 2020
doi: 10.3389/fmats.2020.00017

Resistive Switching in Graphene Oxide

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The search and investigation of resistive switching materials, the most consolidated form of solid-state memristors, has become one of the fastest growing areas in the field of electronics. This is not only due to the huge commercial interest in developing the so-called Resistive Random-Access Memories (ReRAMs) but also because resistive switching materials are gathering way to new forms of analog computation. Unlike in the field of traditional electronics technologies, where Silicon has monopolized most of the applications, the area of solid-state memristors is opened to a broad set of candidates that may contribute to unprecedented applications. In particular, the use of organic-based resistive switching materials can provide additional functionalities as structural flexibility for conformal integration or introduce new and cost-effective fabrication technologies. Following this new wave of organic memristive materials, this work aims at reviewing the existing models explaining the origins of resistive switching in Graphene Oxide, one of the most promising contenders on the battlefield of emerging memristive materials due to its low cost and easy processing methods. Within this manuscript, we will revisit the different theories supporting the phenomenology of resistive switching in this material nourishing the discussion with experimental results supporting the three main existing theories.

Keywords: graphene, graphene oxide, memristor, ReRAM, laser-reduction

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Edited by:
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Reviewed by:
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Kurchatov Institute, Russia

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Specialty section:
This article was submitted to Translational Materials Science, a section of the journal Frontiers in Materials

Received: *24 September 2019*
Accepted: *14 January 2020*
Published: *31 January 2020*

Citation:
Romero FJ, Toral A, Medina-Rull A, Moraila-Martinez CL, Morales DP, Ohata A, Godoy A, Ruiz FG and Rodriguez N (2020) Resistive Switching in Graphene Oxide. Front. Mater. 7:17. doi: 10.3389/fmats.2020.00017

INTRODUCTION

Resistive switching materials are opening a completely new device paradigm in the field of electronics. On the one side, their intrinsic non-volatile memory effect associated with two different high and low resistance states (HRS and LRS, respectively) has suited them for application in the digital domain (Lee et al., 2007; Hong et al., 2010; Zhuge et al., 2010). On the other side, and not less important, they are the right support to develop neuromorphic circuits which can leave out the CMOS-based emulation (Wang et al., 2016; Zu et al., 2019). Resistive switching materials constitute the technology that enables the simple implementation of solid-state memristors, the fourth electrical element that completes the fundamental relations between voltage, charge, current, and flux (Chua, 1971). Their operation is based on the modulation of their resistance according to the bias history of the device. This property allows mimicking biological synapses in a coherent and natural manner (Jo et al., 2010; Zhou et al., 2019). Consequently, resistive switching materials

are of most interest for the implementation of artificial neural networks (Yu et al., 2011; Yu, 2017; Lanza et al., 2018) able to surpass the computation schemes based on the classical von Neumann paradigm.

Inside all the existing memristive solid-sate materials portfolio this short review is focused on one of the most anticipated and promising contenders, Graphene Oxide (GO). Graphene Oxide is a highly functionalized (mainly hydroxyl and epoxide groups) form of graphene that is usually stacked in platelets (Dreyer et al., 2010; Coroş et al., 2019). Its main advantage with respect to its pristine graphene counterpart, comes from its inexpensive and simple processing (Yu et al., 2016). Actually, its defective nature is believed to be the source of its memristive properties (Porro et al., 2015).

GO based memristors have been demonstrated both with planar and vertical structures showing reliable and repeatable resistive switching properties (Khurana et al., 2013; Porro et al., 2015; Hui et al., 2017). Despite the rapid increase in the number of publications related with GO-based memristors, there is not a unique explanation for the origins of the resistive switching, but rather it seems that fabrication parameters such as the choice of deposition technique for GO and electrodes, electrode materials, level of reduction etc., originate different switching behavior and therefore a diversity of explanations of the origins of the switching mechanisms. The different theories to explain the phenomenon can be grouped in three major models that will be rounded up in this short review: (i) metallic-based filamentary conduction, (ii) contact-resistance modification induced by ion drift, (iii) oxidation-reduction mechanisms in the bulk GO.

METALLIC FILAMENTARY CONDUCTION

Metal filament formation has been the preferred mechanism to explain resistance switching in inorganic memristors (Van den Hurk et al., 2015; Mohammad et al., 2016; Li et al., 2017; Wang et al., 2018), but also in organic ones (He et al., 2009; Sparvoli et al., 2019). According to this model, when a positive voltage is applied to the active electrode, the material is oxidized electrochemically and the resulting cations migrate through the insulating layer up to reach the cathode. A filament is originated thanks to this movement of metallic ions, resulting from the oxidation of one of the electrodes that conform the memristor stack (**Figure 1A**). This is particularly observable when using Al electrodes since this is one easily oxidizable metal (Pradhan et al., 2016).

When the ions reach the opposite electrode they gather together and the reduction reaction yields the growth of a metallic strand back to the ion reservoir electrode. When the filament is close enough to the anode, the resistance between the electrodes drops suddenly turning the HRS into the LRS of the device. This mechanism is typically characterized by very abrupt transitions between the current levels. Reversing the bias polarity, and therefore the electric field, causes a reverse diffusion of the metal ions that induce the rupture of the metallic filament.

The metallic filamentary model has been used to explain the resistance switching in thin GO memristors typically in stacked structures in-between to reactive metallic electrodes (Waser and Aono, 2007; He et al., 2009; Porro et al., 2015).

CONTACT RESISTANCE MODIFICATION BY OXYGEN ION DRIFT

Jeong et al. pioneered a work (Jeong et al., 2010) where thin GO films were embedded in-between two Al electrodes showing potential for flexible non-volatile storage on a polyethersulfone substrate. Several experiments supported by X-ray diffraction, High Resolution Transmission Electron Microscopy, and also including the absence of an ohmic behavior, made the authors exclude the existence of a conducting filament in the bulk GO. In this case, the resistive switching is attributed to the formation/destruction of local filaments in the thin insulating layer at the interface between the top Al electrode and the bulk GO film. The authors hypothesized that those filaments were produced by the oxygen ion transfer between an insulating barrier (AlO_x) at the interface of the top electrode in **Figure 1B** and the GO domain. Initially, the Al/GO electrode is expected to be amorphous and non-homogeneous due to the overlap of multiple GO platelets produced by the spin-casting deposition and redox reactions triggered at the interface. This region is expected to be rich in sp^3 insulating domains constituting an insulating barrier that gives rise to the HRS. Under reverse bias polarity, local conductive filaments are grown by field-induced oxygen diffusion into the GO; thus the oxygen returns back to the bulk GO decreasing the insulating barrier and giving rise to the LRS. This model was further confirmed by replacing the electrode with an inert metal (Au) resulting in lack of resistive switching effect.

Several authors have postulated variations of this mechanism, i.e., oxygen ions drift leading to changes on the energy barrier at the interface GO-electrode, as the source of resistive switching in their GO experiments (Wang et al., 2012; Porro and Ricciardi, 2015), and despite the fact that in some cases the model described in Jeong et al. (2010) is not explicitly described (Kim et al., 2019), the resistive switching arguments provided are aligned with this approach.

OXIDATION-REDUCTION MECHANISMS IN THE BULK GO

The third model explaining resistive switching in GO is connected to the drift of functional groups and its impact on the resulting different sp^3 and sp^2 domains on the bulk substrates (Khurana et al., 2013). This is particularly relevant to describe memristance in planar structures or to explain different set, and reset speeds. In this way, resistive switching is connected to a reversible filamentary phenomenon (Wei et al., 2012) in which the conductive path or paths are formed by turning insulating sp^3 domains into conducting sp^2 bonds (oxygen vacancies) based on the detachment of oxygen containing-groups under the action of an electric field, especially in those regions of low conductivity (Qi et al., 2018). This theory finds grounds in different first principles numerical simulation studies that

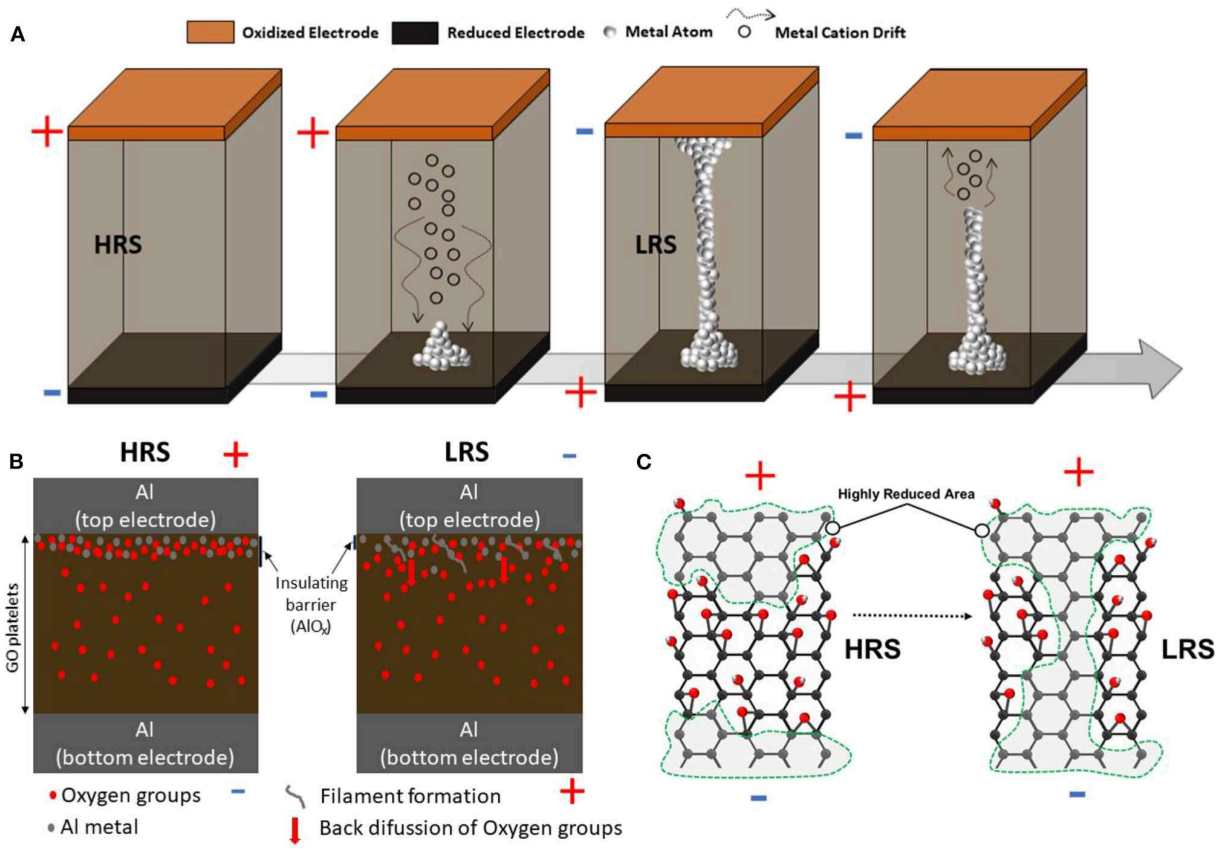

FIGURE 1 | (A) Conceptual representation of the formation and annihilation of a metallic filament responsible for the resistive switching according to the metallic filamentary. **(B)** Model of the resistive switching in graphene oxide [adapted with permissions from Jeong et al. (2010)]. Copyright 2010 American Chemical Society. The as-fabricated device is in the HRS due to the insulating top interface layer formed by a redox reaction between Al and the GO film; The LRS state is induced by formation of filaments at the top interface layer due to oxygen ions diffusion by an external negative bias on the top electrode. **(C)** The GO surface is characterized by the combination of sp^2 (green dashed areas) and sp^3 domains. At a nanoscale level, the sp^2 regions present high-conductivity but they are interrupted by low-conductivity sp^3 domains rich in functional groups. When a current is flowing, the high resistivity of the sp^3 domains creates local large gradients of electrostatic potential resulting in strong local electric fields. Joule heating of the high resistivity region triggers the drift of the oxygen containing groups (migration of functional groups), creating eventually a conductive filament.

demonstrate the formation of domains of highly functionalized Carbon interrupted by low oxidized domains (Kim et al., 2012; Zhou and Bongiorno, 2013); the stoichiometry of those domains is prone to be modified due to the low migration barrier of oxygen in GO (Dai et al., 2013; Zhou and Bongiorno, 2013). **Figure 1C** illustrates this process of resistive switching. The non-uniformity in the number and location of the functional groups of the partially reduced graphene oxide is responsible for the creation of regions of different conductance (or conductive domains). The sp^2 regions present high-conductivity but they are interrupted by low-conductivity sp^3 domains at a nanoscale level. When a current is flowing, the high resistivity of the sp^3 domains create large gradients of electrostatic potential at a local level resulting in strong local electric fields. In this way, and assisted by the action of Joule heating in the switching material, there is a drift of oxygen containing groups that generate changes on the reduction level and therefore on the conductance. A recent experimental work (Romero et al., 2019) further supports this approach relating the memristance of GO with a bulk phenomenon involving the drift of oxygen ions and oxygen-containing groups inducing local changes in the stoichiometry level of the GO. The authors fabricated macroscopic size (∼mm) laser-reduced graphene oxide based memristors concluding that due to the considerable distance between the electrodes and to the fact that under different contact approaches (including also organic electrodes) the resistive switching was present, it was necessary to rule out the creation of metallic filaments or the participation of the contacts in the process. Despite this model may be only appropriate for partially reduced GO, this work commits memristance in GO to the creation of a percolation path of highly reduced GO by the energy accumulated in the device. This theory agrees with the prospective estimation of the energy scale of the phenomenon given in Romero et al. (2019), and it is also supported by Times series Statistical Analysis (Rodriguez et al., 2019): the results thrown from the analysis of successive set and reset processes show that the autocorrelation

and partial autocorrelation levels match those typically found in resistive switching due to a well-defined conductive path between the electrodes that it is interrupted at a Quantum Point Contact (Roldan et al., 2018).

CONCLUSION

The future of memristive devices relies on the development of adequate technologies able to outperform and provide additional value over the existing CMOS mainstream line. Among a plethora of material alternatives, GO based memristors have been pointed by many recent publications as one of the more interesting contenders due to promising switching properties, ultrathin thickness, easy processing approaches and intrinsic structural flexibility. However, there is still a long way to go to become a competitive technology, starting with an in-depth understanding and analytical description of the physical origins of its resistive switching features. There are three main sources of memristance acknowledged in the bibliography: first, considering the formation of a metallic filament due to the electrodes; second, attributing it to the change in the contact resistance, due to oxygen ions diffusion, as the main cause of the resistance changes; and finally, the third model, considering the evolution of the bulk GO conductance due to functional groups migration and the formation of a conductive path (formation of sp^2 conductive domains). Those models share in common that the existence of functional groups in GO is responsible for the resistive switching. However, the ultimate impact of these functional groups on the physics and chemistry of the process is different in each case: metallic filament formation/destruction in the first model, contact resistance variation in the second, and formation of sp^2 conductive paths according to the third model. The existing investigations have not excluded, or considered, the possibility of a combination of the former mechanisms as the source of memristance. In particular, the combination of a metallic filamentary mechanism in conjunction with the contact resistance modification is certainly a possibility whenever metallic electrodes are present. However, the case of an oxidation-reduction in the bulk is rather different, since, as demonstrated experimentally, resistive switching is present in the absence of metallic electrodes. Nevertheless, this model can be considered as another form of filamentary mechanisms, where the filament, in this case, is of an organic nature. For the time being, it is unclear though which one is the predominant mechanism causing the memristance in GO, but rather the experiments show that the particular device configuration (size of the active material, electrodes, and reduction level) determines the ultimate cause for the resistive switching.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

FUNDING

This work has been supported by the Spanish Ministry of Science, Innovation and Universities/FEDER-EU through the project TEC2017-89955P and the pre-doctoral grants FPU16/01451, FPU16/04043, the Junta de Andalucía/FEDER-EU through the project B-RNM-375-UGR18 and the JSPS KAKENHI through grant number JP18k04275.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.