Role of GO and r-GO in resistance switching behavior of bilayer TiO2 based RRAM

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Role of GO and r-GO in resistance switching behavior of bilayer TiO$_2$ based RRAM

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Abstract

Graphene-based resistance random access memory devices (RRAMs) have shown promise as a suitable replacement for flash memories, owing to their fast switching speed, low programming voltage, better scalability and great reliability. Furthermore, recent research works have shown bi-layer RRAM devices exhibiting better performance along the same parameters, where titania is one of the most commonly used materials. In the present work, we have studied the resistance switching behavior in a bi-layer RRAM device structure of TiO$_2$ with graphene oxide (GO) and reduced graphene oxide (rGO). Switching mechanism in these devices has been investigated by detailed experimental characterization in conjunction with a finite element modeling (FEM) simulation. A dual conical conductive filament has been used in the present work, based on the modeling of the electroforming process carried out by FEM. It has been demonstrated that for the GO/TiO$_2$ based hybrid RRAM device structure, GO acts as an active filament formation layer, whereas in the rGO/TiO$_2$ bi-layer structure, rGO acts as a mere electrode.

Keywords: RRAM, bi-layer oxides, graphene

(Some figures may appear in colour only in the online journal)

Introduction

Non-volatile memories (NVMs) are essential to the electronics industry. The most widely used NVM, flash memory, is reaching a physical limit, which has motivated the search for alternative memory devices. Resistance random access memory (RRAM) devices have come up as one of the most suitable replacements in recent years. Compared to flash memories, they have extremely fast switching speeds, lower programming voltage, better scalability, and great reliability [1].

A wide range of materials such as transition metal oxides (e.g. HfO$_2$ [2], TiO$_2$ [3], Al$_2$O$_3$ [4], Ta$_2$O$_5$ [5], ZnO [6], VO$_2$ [7], etc.), perovskite oxides (e.g. SrTiO$_3$ [8], YMnO$_3$ [9], etc.) and chalcogenides (e.g. Ag/Ge$_{0.25}$Se$_{0.75}$, Ge$_2$Sb$_2$Te$_5$ [10], etc.) have been found to show resistive switching. A typical device structure of an RRAM contains a switching layer sandwiched between top and bottom electrodes. Recent research works have shown that devices with bilayer oxide configuration exhibit enhanced switching speed [11], endurance [12], retention [13], and lower switching voltage [14], as compared to single layer devices.

A variety of carbon-based materials, like oxygenated amorphous carbons [15], amorphous carbons [16] and graphene oxide (GO) [17], too, have shown resistive switching behavior in recent times. Among many attractive features of these RRAMs, forming-free behavior, flexibility, and multilevel-switching make carbon-based RRAMs desirable [18]. Recently, a comprehensive study [18] on graphene based RRAMs has predicted that although GO and reduced graphene oxide (rGO) have shown some promise, they should be combined with other materials in bi-layer RRAM to further improve their performances [18–21]. One of the most important aspects of carbon-based RRAMs is their high temperature retention (∼250°C) [22], which makes them attractive for application in harsh environments. Table 1 summarizes the performances of carbon-based (GO, rGO and graphene) RRAMs in comparison with other RRAMs, based
<table>
<thead>
<tr>
<th>Table 1. Comparison of carbon-based RRAMs with TMO based RRAMs.</th>
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<tbody>
<tr>
<td><strong>Device structure</strong></td>
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<tr>
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<tr>
<td><strong>CARBON-BASED</strong></td>
</tr>
<tr>
<td>ITO/GO/Ag</td>
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<tr>
<td>PEN/Ti/Pt/GO/Ti/Pt</td>
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<tr>
<td>Al/GO/ITO</td>
</tr>
<tr>
<td>Ag/ZrO/SLG/Pt</td>
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<tr>
<td>Al/PFCF/GO/ITO</td>
</tr>
<tr>
<td>Pt/Ti/GO/Pt/Ti</td>
</tr>
<tr>
<td>G/TiO₂/Al₂O₃/TiO₂/G</td>
</tr>
<tr>
<td>TiN/HfO₂/G/Pt</td>
</tr>
<tr>
<td>Pt/GO/PCMO/Pt</td>
</tr>
<tr>
<td>Al/Au/P3HT/Al/ZnO-G QDs/Al/SiO₂/Si</td>
</tr>
<tr>
<td><strong>TMO-BASED</strong></td>
</tr>
<tr>
<td>Pt/HfO₂/Ta</td>
</tr>
<tr>
<td>Pt/Ta₂O₃/Ta₂O₅/Pt</td>
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<tr>
<td>TiN/HfO₂/HTN</td>
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<tr>
<td>Ta/αSi/Al₂O₃/Cu</td>
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<tr>
<td>Pt/Ta₂O₃/Pt</td>
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<tr>
<td>Pd/Gd₂O₃/Pt</td>
</tr>
</tbody>
</table>

*PEN = polyethylene naphthalate (SLG = single layer graphene) (PFCF = polymeric fluorocarbon) (P3HT = polythiophene) (QD = quantum dot) (PCMO = Pr₀.7Ca₀.3MnO₃).
on Si and transition metal oxides (TMO), reported in the literature. Although research on GO and rGO based RRAM devices have been initiated very recently, there has been significant progress in terms of device performance. However, there is much more scope for improvement in factors such as data retention, endurance etc. More importantly, the resistive switching mechanism in these carbon-based RRAMs has been poorly understood.

GO heterostructure with polyvinylidene difluoride (PVDF) electrodes—PVDF/GO/PVDF [23] has been considered, where the observed bipolar switching has been attributed to the formation and breakage of oxygen vacancy conduction filament. A composite GO-based RRAM has also been reported with TiO₂ nanoparticles [24], where the switching has been attributed to electron trapping and de-trapping in the composite film. Recently, Pt/GO/Ti/Pt-based RRAM device structures have shown excellent endurance and retention performance, along with faster switching (sub 5 ns) speed [19]. They have attributed the resistive switching mechanism to redox reactions in the Ti/GO interface, resulting in the formation of TiOₓ in the interface layer.

However, bilayer configuration consisting of TiO₂ and GO or rGO has never been reported in literature. Although, TiO₂ has been investigated extensively as a single layer structure. Moreover the advantage of better scalability and switching speed have been reported, when TiO₂ has been used in a bi-layer RRAM device structure with TaOₓ [37], SiOₓ [38], Al₂O₃ [39], HfO₂ [40] etc. Hence, we have chosen TiO₂ in the present work to investigate the switching mechanism of bi-layer RRAM. Although GO or rGO based memories have been investigated in the recent past [18], the switching mechanism of GO reported in literature is somewhat conflicting and confusing. Moreover, several questions remain unanswered as of today: (a) what is the specific role of GO/rGO in the resistive switching process? (b) Does the switching take place due to bulk mechanisms in the switching layer, or properties of interface with electrode or buffer layer? (c) Are they playing the role of electrode, filament formation layer or oxygen vacancy reservoir?

In the present work, an attempt has been made to answer these questions, regarding the specific role of GO and rGO in the bilayer device configuration with TiO₂. Two separate device structures have been fabricated: W/GO/TiO₂/FTO and W/rGO/TiO₂/FTO, where fluorine-doped tin oxide (FTO) acts as the bottom electrode deposited on glass substrate. Furthermore, to understand the switching mechanism in these bilayer RRAM device structures, a finite element modeling (FEM) simulation has been carried out using COMSOL Multiphysics software. Since the migration of oxygen vacancies plays a dominant role in the switching behavior of GO-based RRAMs [18, 25], the filamentary model [3, 5, 23, 41, 42] has been widely used to understand the underlying switching mechanism. Furthermore, an electroforming process has been simulated using FEM. To the best of our knowledge this is the first report on the temporal profile of the electroforming process demonstrated by COMSOL FEM.

Based on the simulation results of electroforming, a dual conical conductive filament model has been utilized for the switching mechanism, as demonstrated in figure 1. In this report, we have shown that simulation corroborates with experimental data when GO acts as the filament formation layer in the W/GO/TiO₂/FTO device structure, where TiO₂ acts as the reservoir of oxygen vacancies. On the other hand, rGO acts as an electrode in the W/rGO/TiO₂/FTO structure, where TiO₂ acts as the filament formation layer.

![Figure 1. Device configurations modeled using dual-conical filaments in active layers.](image-url)
Experimental

Materials

Graphite powder (100 mesh, 99.9995%), hydrogen peroxide (H₂O₂, 30%), sodium nitrate (NaNO₃, 99.0%), potassium permanganate (KMnO₄, 99.0%), sulfuric acid (98%), hydrazine hydrate (50%–60%), ammonium hydroxide solution (NH₄OH, 25% in H₂O), Whatman 41 filter paper, titanium isopropoxide (Ti[OCH(CH₃)₂]₃), TTIP 97%, absolute ethanol, hydrochloric acid (37%) and FTO coated glasses (~13 Ω, TEC15) have been purchased. All the reagents have been used without any further purification.

Synthesis

\[
\begin{align*}
\text{K Mn O}_4 + \text{H}_2\text{SO}_4 &= \text{K}^+ + [\text{MnO}_4]^2- + \text{HSO}_4^- \quad \text{(1)} \\
2\text{HMnO}_4 &= \text{Mn}_2\text{O}_7 + \text{H}_2\text{O} \quad \text{(2)} \\
2\text{NaNO}_3 + \text{H}_2\text{SO}_4 &= \text{Na}_2\text{SO}_4 + 2\text{HNO}_3 \quad \text{(3)} \\
\text{Mn}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 &= [\text{MnO}_4]^2+ + [\text{HSO}_4]^2- + \text{H}_2\text{O} \quad \text{(4)}
\end{align*}
\]

To prepare graphite oxide, a modified Hummers’ technique [43] has been employed. Graphite powder (1 g) and NaNO₃ (0.5 g) have been mixed in 2:1 ratio on an ice-water bath. 23 ml sulfuric acid has been added drop-wise with simultaneous stirring, followed by 3 g KMnO₄. After 20 min, the ice-water has been removed. The slurry has been diluted with warm deionized (DI) water, followed by heating at 90 °C for 30 min. 30% H₂O₂ has been added dropwise to the slurry until the bubbling disappeared, resulting yellow solution. The filtrate has been centrifuged to make the pH neutral. Then, the thick slurry has been lyophilized to get graphite oxide flakes.

Graphite oxide slurry (10 mg in 100 ml H₂O) has been sonicated for 2–3 h. 315 μL 25% NH₄OH has been added, followed by 35 μL hydrazine hydrate. After 10 min in the ambient atmosphere, it has been refluxed for 4 h, at 90 °C and centrifuged at 7000 rpm for 20 min before drying.

A titania compact layer has been fabricated from titania sol prepared by mixing 175 μL TTIP dropwise to 1.25 ml ethanol. Separately, 17.5 μL 2N aq. HCl solution has been mixed with 1.25 ml ethanol. The TTIP-ethanol solution has been added to the HCl-ethanol solution drop-wise with simultaneous stirring. Before the deposition, the solution has been sonicated followed by filtration (PVDF syringe filter) [44].

Device fabrication

All the studied thin film samples have been fabricated on FTO coated glass substrates (20 mm × 20 mm). The glass substrates are washed by sonication with soap (Hellmanex III) in warm DI water (v/v = 2:100) followed by isopropanol and acetone/water mixture (v/v = 1:1). Before the deposition, substrates have been treated in a UV–O₃ chamber for 10 min [45].

A spin coating technique has been used to obtain all the thin film samples. 60 μL titania sol has been dispensed on FTO coated glass substrate, rotating at 4500 rpm for 30 s. Then, the annealing of TiO₂ film has been carried out at 500 °C for 4 h. A 2.5 °C min⁻¹ heating rate has been followed with 10 min holding at 125 °C, 200 °C, 300 °C, and 400 °C. GO (10 mg/100 ml, aq) and graphene (10 mg/100 ml, aq) have been spin coated at 4000 rpm for 30 s, followed by annealing at 80 °C for 10 min.

Characterization

The thickness of the as-fabricated thin films has been measured using an optical profilometer (Bruker GT-KO). The thin film samples have been characterized by x-ray diffraction (XRD) and Raman spectroscopy techniques using a PANalytical x-ray diffractometer XPERT PRO and Action Spectra Pro SP-2500, respectively. A 532 nm laser of 50 mW power with 10% intensity has been used for recording the Raman spectra in the range of 700–3500 cm⁻¹. I–V measurements have been carried out using a Signatron 1160-6N probe station with a heating stage connected to Keithley 4200-SCS semiconductor parameter analyzer.

Device simulation

There are multiple theories for switching mechanisms in resistive switching devices. We have carried out the device simulation using a conductive filament model, which is one of the most popular theories of resistance switching [46, 47] and it has conformed to our experimental data. FEM in COMSOL Multiphysics software has been utilized for the simulation. It has been assumed that the active switching layer in the device constitutes a ‘dual conical conductive filament’ made of oxygen vacancies in the oxide layer, as proposed by Kim et al [3]. It is a simplified geometry of the complex non-linear curvature of the actual filament, which utilizes discontinuous cone geometry, with different slopes for the two sections of the dual-cone. Since the weakest (thinnest) part of the filament will invariably be the one to rupture, such simplified ‘dual conical’ geometry should yield accurate results, where the thinner section ruptures and the wider section remains intact. Representation of the model can be seen in figure 1. FEM of the electroforming process has also been performed, which further validates the assumed geometry.

GO contains sp³ –C–C– bonds due to the oxidation. Oxygen breaks the regular graphitic sp² –C–C– network and forms out of plane or C–O–C– bonds. Conductivity can be gradually increased by the removal of oxygen. The reduction of GO decreases the number of out of plane bonds, and rGO retains its regular sp² –C–C– bonds with fewer sp³ C–C bonds [48, 49]. The dangling bonds in rGO act as oxygen vacancy sites providing higher conductivity. We have used this idea to develop a model of conductivity, which increases with an increase in the concentration of oxygen vacancies. Hence, the models of electrical and thermal conductivities have been developed as functions of oxygen vacancy concentration. The electrical conductivity of almost zero is taken for GO with no oxygen vacancy concentration, and conductivity similar to that of rGO is taken at high
been used directly as the top electrode. In the I–O
oxygen vacancy concentrations. Such concentration-depen-
ments, the tungsten probe has been kept in direct contact with
the oxide layer. A probe-tip has been previously used as the
top electrode to develop ‘top-electrode free’ memristors [50–53]. Hence, the problem of oxygen affinity with the
electrode is minimized. Since the electrode is not permanently
deposited on the oxide layer, the time of contact between the electrode and the dielectric layer is limited. This limited time
of contact of the tungsten probe with the oxides is a reason
why interface red-ox reactions have been neglected in the
simulation model, with the filamentary process dominating the
resistance switching.

Modules and equations used in COMSOL Multiphysics
software are the coefficient form of the partial differential
PDE module has been utilized to account for the generation
in the oxide layer during the electroforming process. The coefficient form of the
PDE module has been utilized to simulate ‘Fick’s diffusion’
and ‘Mott–Gurney migration’ [54]. At an atomistic level, ionic migration corresponds to ions hopping from one site to
another. In the absence of an electric field, this hopping is
random. If an electric field is applied, then a net ion flux
occurs, which is estimated using Mott–Gurney Law. Since
these phenomena are confined to the oxide layer, so is the
coefficient form of the PDE module. The electric currents
module has been used to control the voltage profiles on the
devices, and observe the resultant electric field, current and
current continuity: \( \nabla \cdot \sigma \nabla V = 0 \) ... (6)
Joule heating: \( \nabla \cdot k_{\text{eff}} \nabla T = j.E = \sigma |\nabla V|^2 \) ... (7)

The equations involved are as follows.

\[
\frac{\partial N}{\partial t} = \nabla \cdot (D \nabla N - \nu N) + G \ldots \tag{5}
\]

Mott–Gurney electro-migration velocity:
\[
\nu = a \cdot f \cdot \exp \left( \frac{E_a}{kT} \right) \sinh \left( \frac{q\nu E}{2kT} \right) \ldots \tag{8}
\]
generation term: \( G = A \cdot \exp \left( -\frac{E_b - q\beta E}{kT} \right) \ldots \tag{9} \)

\( N \) = concentration of diffusing species; \( D \) = diffusion coefficient; \( J \) = mass flux, \( \sigma \) = electrical conductivity; \( \nu \) = hopping
distance; \( f \) = vibration frequency; \( E_a \) = activation energy for diffusion; \( E_b \) = activation energy for diffusion; \( \lambda = \) = pre-exponential
factor of generation term; \( \beta = \) simulation mesh size; \( E_b \) = energy barrier for ion hopping; \( q\nu E \) = barrier reduction
due to field application [41, 42].

Equation (5) gives us oxygen vacancy concentration
iteratively, which is used to obtain the thermal conductivity
and electrical conductivity. These are used to calculate the
current for a given voltage, through equations (6) and (7).
Oxygen vacancy concentration-dependent models have been
used for the parameters involved. The concentration-depend-
ent models of electrical conductivity and thermal conduc-
tivity have been provided in figure 2.

For GO, a thermal conductivity plot has been obtained
based on [55], and an electrical conductivity plot has been
calculated from the sheet resistance and film thickness measured
in [56]. For titania, the thermal conductivity values have been
estimated from the range obtained from [57–59], and the
electrical conductivity pre-exponential factor (\( \sigma_0 \)) of the
Arrhenius equation has been estimated from [60, 61], with
maximum value reaching 10,000 S m\(^{-1}\) [61]. The profile of \( \sigma_e \)
curves has been obtained through cubic interpolation of conductivity
data points calculated from known values of current and voltage. The models thus shown in figure 2, have been utilized in the expression of electrical conductivity:

\[
\sigma = \sigma_e \exp \left( -\frac{E_a}{kT} \right) \]

The concentration-dependent thermal conductivity model
\( k_{\text{th}}(N) \) has been used directly.

The mobility of oxygen ions (and hence, oxygen vacancies)
has been calculated through the Einstein’s electric mobility
\[
\mu = \frac{qD}{kT},
\]
where \( D \) = diffusion coefficient, \( k \) = Boltzmann constant, \( \mu \)
is mobility, \( q \) = ionic charge. The diffusion coefficient is
obtained through the Arrhenius form of the equation:

\[
D = D_0 \exp \left( -\frac{E_a}{kT} \right).
\]

\( D_0 \) = pre-exponential factor, \( E_a \) = activation energy.
Additionally, the forming process involves the electrochemical Butler–Volmer equation [62].

\[ i_{BV} = i_0 \left( C_R \exp \left( \frac{\alpha_c F \eta}{RT} \right) - C_a \exp \left( \frac{-\alpha_a F \eta}{RT} \right) \right) \]  

where, \( i_{BV} \) = Butler–Volmer electrode current density; \( i_0 \) = exchange current density; \( F \) = Faraday constant; \( \alpha_c \) = dimensionless cathodic charge transfer coefficient; \( \alpha_a \) = dimensionless anodic charge transfer coefficient; \( \eta \) = activation over-potential.

The Butler–Volmer equation provides the total current at an electrode, due to electrochemical redox reactions. It equates the net current of cathodic and anodic reaction currents. Equation (10) has been used to obtain the current density of the oxygen vacancies obtained due to the reduction of oxide material near the bottom electrode, aided by the Joule heating process. These vacancies travel towards the top electrode due to Fick’s diffusion, Mott–Gurney electromigration, and Butler–Volmer current, occurring due to the concentration gradient of vacancies and negative forming voltage, respectively. The results are shown in figure 4 for the W/GO/TiO2/FTO device. The data validates the assumption of a ‘dual conical’ geometry.

Earlier works have presented a forming process through kinetic Monte Carlo simulations [63], a code of Mott-resistor network [64], etc. However, a simplified FEM model of electroforming has been presented using COMSOL Multiphysics for the first time in the present work.

Results and discussion
The quality of thin films of GO, rGO, and TiO2 have been investigated by XRD and Raman spectroscopy. For graphite

Figure 3. (a) Room temperature Raman spectra of lyophilized GO and rGO. (b) XRD patterns of GO/TiO2/FTO and rGO/TiO2/FTO.

Figure 4. 2D Temporal development of the oxygen vacancy concentration profile, presenting filament formation during electroforming (−10 V) in W/GO/TiO2/FTO device structure.
derivatives, Raman spectroscopy is an inevitable tool. Raman spectra demonstrate the structural changes that happened from pristine graphite to GO. Figure 3(a) depicted the 532 nm Raman spectra of GO and rGO flakes. In GO, the G band appeared at 1595 cm$^{-1}$. But the G band red shifted to 1584 cm$^{-1}$ in rGO spectra. G band is the representative of sp$^2$ carbon network. It occurred due to the first order phonon scattering (E$_{2g}$ mode) of sp$^2$ carbon network. Whereas, D band appeared at 1348 cm$^{-1}$ of GO Raman spectra, due to the K point phonons of A$_{1g}$ symmetry. In rGO, D band appeared at 1351 cm$^{-1}$. D band signifies the out of plane vibrations for the defects present in the GO. As mentioned above, reduction of GO decreases the number of out of plane bonds; rGO retains its regular sp$^2$–C–C– bonds with less number of sp$^3$ C–C bonds.

$$La = (2.4 \times 10^{-10}) \lambda^4 (I_D/I_G)^{-1} \ldots$$

(11)

The increase in the I$_D$/I$_G$ value, compared to GO in the Raman spectrum of rGO, can be attributed to the increase in the number of sp$^2$ domains, and the decrease in the individual crystallite size of the sp$^3$ domains, since the crystallite size is inversely proportional to I$_D$/I$_G$, as demonstrated in equation (11) [48, 49, 65].

XRD profiles of the thin film layered structures are illustrated in figure 3(b). Both the profiles have exhibited a peak at 2$\theta$ = 25.8 and 37.7 degrees [66, 67], which correspond to the (101) and (004) planes, respectively, of the anatase TiO$_2$ structure. The peak corresponding to the (001) plane of GO has been detected at 10.9 degrees in the TiO$_2$-GO sample. Whereas, at 24.9 degrees a blunt peak has appeared in the TiO$_2$-rGO sample, which corresponds to (002) plane of rGO. Observed other XRD peaks have been yielded from the FTO coated glass substrate.

Electroforming has been carried out at a negative bias of $-10$ V for both the devices. As discussed above, Fick’s diffusion, Butler–Volmer current, Mott–Gurney drift and Joule heating have been utilized for FEM of the forming process. Results have been presented in figure 4. The development of oxygen vacancy filament has been presented from left to right. The top electrode has a negative bias of $-10$ V, while the bottom electrode is grounded. The two layers of materials presented in figure 4 correspond to GO at the top and titania at the bottom, acting as a buffer layer. It can be observed from the final shape of the filament that the dual-conical geometry can be taken as a suitable approximation for the filament.
geometry. The I–V characteristics have been obtained after the forming process.

To study the switching mechanisms, I–V measurements have been carried out for both the device structures, i.e. W/GO/TiO₂/FTO and W/rGO/TiO₂/FTO. For the W/GO/TiO₂/FTO sample, a voltage sweep of 0 → 2.5 V → −2.5 V → 0 V has been done, with W being the top electrode. We obtained the I–V characteristics as shown in figure 5(a).

Further, to validate this experimental result, a dual-conical conducting filament model has been adopted through its simulation in COMSOL Multiphysics software. The oxygen vacancies have been simulated to migrate from the TiO₂ to a high resistance state (HRS) to a low resistance state (LRS). Simulation of oxygen vacancy breaking after RESET.

Figure 7. (a) I–V characteristics of simulated and experimental work for W/rGO/TiO₂/FTO, assuming TiO₂ as active layer, (b) proposed geometry of filament formation in TiO₂ layer, (c) 3D representation of filament, (d) oxygen vacancy concentration at t = 0, (e) filament breaking after RESET.

Hence, it validates our proposed switching mechanism based on the assumption that in W/GO/TiO₂/FTO, GO acts as the active layer.

In the case of the W/rGO/TiO₂/FTO device, a voltage sweep of 0 → 10 V → 0 V has been carried out, with W as the top electrode. On performing the I–V characterization experiment, we obtained a sharp RESET at 7.75 V. To validate these results, FEM simulation has been undertaken, assuming rGO as the active layer. However, the simulations have not matched the experimental data, as evident from figure 6.

Figure 6 shows that assuming rGO as the active layer yields theoretical results deviating widely from experimental results. Furthermore, the experimental data of W/rGO/TiO₂/FTO shows that the RESET for the rGO sample occurs at a much higher voltage (7.75 V) than that for the GO sample (2.2 V). If rGO has been the active layer in the rGO-TiO₂ bilayer, then the switching voltage should have been lower than in GO-TiO₂, owing to higher conductance and charge carrier mobility of rGO. Based on these observations, i.e., mismatch of experimental and simulation data, and higher RESET voltage for the rGO based device, we have proposed that rather than rGO, it is the titania layer which acts as the active layer. This is interesting because a simple reduction of GO layer in the GO-TiO₂ bilayer yields rGO-TiO₂, a device with a GO-TiO₂ bilayer yielding a rGO-TiO₂, a device with ~3 times higher switching voltage, and an entirely different switching layer. The model consists of a dual-conical oxygen vacancy conducting filament used for the Magnéli phase of titania, i.e. TiOₓ, which forms due to localized Joule heating [68–70]. The conductive rGO layer has been assumed to be part of the top electrode stack (W/rGO). The axisymmetric geometry used for the device is shown in figure 7(c).
The electrical conductivity of the TiO$_2$ surrounding the TiO$_2$ filament is taken to be much lower, which enables the majority of current to pass through the filament. Hence, on breakage of the filament during RESET, as shown in figure 7, the current drops sharply, putting the device in OFF state. The simulated I–V characteristic of the device is displayed in figure 7(a). The inset figure presents the simulated temporal resistance. Since a single conducting path model has been used in our simulations, we have multiplied the current obtained by a factor of 900 to match with experiments. This indicates that in the rGO-TiO$_2$ sample, 900 filaments have been forming and breaking simultaneously, similar to the observations by Kim et al [3]. By changing our assumption of active layer during simulation, a decent match with the experimental data is obtained. We have obtained a higher switching voltage, sharper switching and higher HRS/LRS ratio, resulting in greater coherency with experimental I–V characteristic, as evident in figure 7(a). This is a testament of the role of rGO as an electrode in rGO/TiO$_2$ configuration. So, it can be concluded that GO is a better option for a hybrid RRAM device structure based on TiO$_2$.

Conclusion

In conclusion, a bi-layer device configuration has been used to gain insight into the individual roles of GO and rGO in the switching process of RRAM. A 2D dual-conical filament model has been used to numerically solve a set of PDEs, in order to obtain resistance switching in RRAMs to validate our experimental results. FEM has been performed to demonstrate the electroforming process using COMSOL, which has shown the signature of dual-conical filament geometry. A simulation using a oxygen vacancy filament formation and breakage assisted switching model has yielded matching results with experiments. Finally, GO has been found to be the active layer in the GO/TiO$_2$ bilayer, while rGO has been observed to act as a mere electrode in the W/rGO/TiO$_2$/FTO configuration. Furthermore, the present work validates the conductive filament model to understand the switching mechanism of a variety of samples, including GO and rGO based RRAMs.

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