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A Graphene-Based Non-Volatile Memory

Loïc Loisel^{a,b,c,†}, Ange Maurice^{a,b,†}, Bérengère Lebental^{c,d}, Stefano Vezzoli^e, Costel-Sorin Cojocaru^c, Beng Kang Tay^{a,b}

^aElectrical and Electronics Engineering, Nanyang Technological University, Singapore

^bCNRS-International NTU Thalès Research Alliance, Singapore

^cLPICM, UMR 7647, Ecole Polytechnique-CNRS, France

^dUniversité Paris-Est, IFSTTAR, France

^eCenter for Disruptive Photonic Technologies, Nanyang Technological University, Singapore

[†] Both these authors contributed equally to the work

ABSTRACT

We report on the development and characterization of a simple two-terminal non-volatile graphene switch. After an initial electroforming step during which Joule heating leads to the formation of a nano-gap impeding the current flow, the devices can be switched reversibly between two well-separated resistance states. To do so, either voltage sweeps or pulses can be used, with the condition that $V_{SET} < V_{RESET}$, where SET is the process decreasing the resistance and RESET the process increasing the resistance. We achieve reversible switching on more than 100 cycles with resistance ratio values of 10^4 . This approach of graphene memory is competitive as compared to other graphene approaches such as redox of graphene oxide, or electro-mechanical switches with suspended graphene. We suggest a switching model based on a planar electro-mechanical switch, whereby electrostatic, elastic and friction forces are competing to switch devices ON and OFF, and the stability in the ON state is achieved by the formation of covalent bonds between the two stretched sides of the graphene, hence bridging the nano-gap. Developing a planar electro-mechanical switch enables to obtain the advantages of electro-mechanical switches while avoiding most of their drawbacks.

Keywords: Graphene, Electro-Mechanical Switch, Non-volatile Memory, Electrical Breakdown, Nano-Gap

1. INTRODUCTION

Since the first developments of the transistor, researchers and engineers have always been able to increase the computing power of electronic chips by increasing the transistor surface density. However, this approach is expected to hit a wall soon, as transistor sizes have decreased to only a few nanometers today (14 nm), closer than ever to the atomic limit.¹ Consequently, new approaches to electronics are actively pursued.

The discovery of graphene in 2004² was deemed very promising because graphene has a much better electrical conductivity than silicon. However, in more than 10 years, no solution has been found to overcome graphene's lack of a bandgap, rendering useless its application as a field-effect-transistor.

Today, researchers are looking for new ways to use the amazing properties of graphene. For example, several graphene-based approaches to memory have been uncovered. Redox memories based on graphene oxide have been demonstrated;³ graphene has also been successfully used as the gate material⁴ in floating gate transistors; electro-mechanical approaches were also developed, where suspended graphene is used as a movable electrode.⁵ One of the most promising approaches to graphene-based memories is the fabrication of nanogap-controlled memories. After an initial electroforming step leading to the propagation of a nm-sized crack impeding the flow of charge carriers, it has been shown that two-terminal graphene memories can readily switch between well-separated resistance states.^{6,7}

Here, we use the same approach to develop two-terminal graphene memories, but instead of using electron-beam lithography to make nanometer-sized devices, we use optical lithography to pattern micrometer-sized

Further author information: (Send correspondence to L.L.)

L.L.: E-mail: loic001@e.ntu.edu.sg, Telephone: +65 93 51 21 07

A.M.: E-mail: maur0003@e.ntu.edu.sg

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devices. This enables us to better characterize the mechanisms at stake, be it electrically (because higher currents are generated) or in terms of surface morphology (AFM) because the affected areas are larger. We interpret the results of these characterization steps by proposing a new model to graphene two-terminal switching: we suggest the memories we developed are based on an electro-mechanical switch. The only fundamental difference between our approach and suspended electro-mechanical graphene memories is that the stability in the ON state is insured by covalent bonds rather than van der Waals bonds.

2. EXPERIMENTAL METHODS

We use monolayer CVD-graphene on Si/SiO₂ (SiO₂: 285 nm) purchased from Graphene Supermarket. First, graphene stripes (of widths 2, 5, 8, 15 μm) are patterned by UV lithography. Then, a second lithography step followed by a lift-off is used to pattern electrodes made of Ti/Au (10nm/100nm). Electrical characterizations are conducted in a Keithley 4200-SCS Semiconductor Characterization System at low pressure (2.10^{-5} to 5.10^{-5} mBar). AFM characterization is conducted with an Asylum Research Cypher S microscope in tapping mode.

3. RESULTS AND DISCUSSIONS

3.1 Electrical breakdown of the pristine devices

Prior to being used as reversible non-volatile switches, the two-terminal devices are electroformed by being subjected to a high voltage sweep (Figure 1). At low voltages, in many devices we realize that the I-V curve is not linear (Stage (1)) despite the fact that graphene is a semimetal and should exhibit an Ohmic behavior. This anomaly is confirmed by the fact that the low-voltage resistance does not scale linearly with L (the distance between the electrodes) or the inverse of W (the width of the graphene strip).

At higher voltages, the I-V characteristic becomes more linear (Stage (2)) and when plotting the resistance values measured at higher voltages against L or 1/W, we obtain linear trends, as expected for graphene two-terminal devices. We explain this behavior by accounting for the contact resistances, which are found to decrease from Stage (1) to Stage (2). During sweeping, the Joule effect leads to rising temperatures at the contacts, which in turn leads to removal of impurities or increase of the contacting surface. Current annealing of graphene has already been demonstrated⁸ to improve its quality. Moreover, thermal annealing is routinely conducted by researchers working on graphene electronic devices.⁷ Conducting two subsequent voltage sweeps (without electrical breakdown) enables to confirm the fact that current-annealing leads to a more Ohmic behavior.

In Stage (3), the conductance increases, leading to a superlinear I-V characteristic. This superlinear behavior has already been reported in graphene devices⁹ and is assigned to temperature-assisted generation of charge carriers. The occurrence of this phenomenon suggests that high temperatures are achieved in Stage (3).

In Stage (4), the conductance decreases drastically at first, leading to a negative differential resistance. This is the onset of electrical breakdown, a phenomenon that has been reported several times in carbon nanotube¹⁰ or graphene devices.¹¹ At $\approx 12\text{V}$ and 14V , two important conductance drops are observed, with the second one leading to a permanent large resistance increase (electroforming).

Resistance values after electroforming are very large, and low-voltage current levels are either undetectable (less than 1 pA at 1V) or very low (Figure 2). When current levels are detectable, the low-voltage I-V characteristics tend to be non-linear. We obtain the best fits of these data by using the Simmons model for tunneling^{12,13} (equation 1):

$$j \approx \frac{e}{2\pi\hbar d^2} \left[(\phi - \mu_L) \exp(-2d \frac{\sqrt{2m(\phi - \mu_L)}}{\hbar}) - (\phi - \mu_R) \exp(-2d \frac{\sqrt{2m(\phi - \mu_R)}}{\hbar}) \right] \quad (1)$$

where j is the current density, e is the electron charge, h the Planck constant and $\hbar$ the reduced Planck constant, d is the barrier size, ϕ the barrier energy, μ_R and μ_L the chemical potentials of the right and left side of the tunneling barrier, and m is the electron mass. To fit the electrical data and extract values for d and ϕ , we set $\mu_L = qV/2$ and $\mu_R = -qV/2$ (the total potential drop across the barrier is V).

Figure 1. Electrical breakdown: I-V curve of a two-terminal device showing four stages. In Stage (1), the current rise is non-linear due to large contact resistances. In Stage (2), the I-V characteristic is more linear because current-annealing led to better contacts. In Stage (3), the I-V behavior is superlinear due to thermal emission of extra charge carriers. Stage (4) is the onset of electrical breakdown.

Figure 2. Low-voltage electrical characteristic of a two-terminal device after electroforming showing very low current values and non-linearity. This behavior is best fitted by a Simmons model for tunneling (red dashed line) enabling estimations of the barrier size and energy. Fitting parameters: d (barrier size) = 1.7 nm, ϕ (barrier energy) = 11 eV.

This model applies to cases where charge carriers tunnel through a potential energy barrier. To do so, the barrier must be small so that the charge carrier wavefunctions extend beyond it. The Simmons model for tunneling enables to estimate values for the barrier size and its height (energy).

Hence, electrical results suggest that electrical breakdown occurs via the formation of an energy barrier for the charge carriers, impeding their flow and resulting in the very large resistance values observed.

3.2 AFM characterization of electroformed two-terminal devices

To obtain more information about what happens during electroforming, we obtain AFM images of the surface after electroforming (Figure 3). It is consistently found that a trench appears during electroforming. Despite

Figure 3. AFM characterization of the surface morphology after electroforming. (a) Height image showing a deep trench. Scale bar: 40 nm. (b) Plot of the 1D height section data showing that the trench is more than 4 nm deep. (c) Proposed matter distribution explaining the AFM data.

the fact that the graphene is monolayer and should not appear much higher than ≈ 1 nm,¹⁴ we consistently find depths larger than 1 nm. By conducting further AFM characterization on the pristine devices (measuring the graphene step height by comparing its height with that of the surrounding SiO₂), we find that most of our devices are covered by a thin layer of resist (few nm). Figure 3 (c) is a schematic possibly explaining the height profile of Figure 3 (b).

While a trench is formed in the resist and the graphene, we also often find that the electroforming process digs a trench in the SiO₂ substrate, much like reported in other references.⁷ It is not so surprising considering the energy of the graphene bonds as compared to the SiO₂ bonds: if the temperature is high enough to create a physical crack in the graphene (by sublimation), it should be high enough around it to damage the substrate.

Hence, the AFM data enable to conclude that during electroforming, a physical crack is created and propagates until the graphene stripe is split in two parts. Crack formation and propagation is actually a well-known phenomenon for electrical breakdown of carbon allotropes.¹⁵

3.3 Electrical switching of the electroformed devices

After electroforming, we find that devices can be switched back to a low-resistance-state (LRS) by applying a voltage sweep or pulse in vacuum (Figure 4). At low voltages the current increases in a non-linear manner because it is mostly driven by tunneling. At higher voltages however, we observe large conductance jumps that are found to be non-volatile even though the conductance is not immediately stabilized (see region > 19 V for the black curve and > 9 V for the green curve in Figure 4 (a)).

For the conductance to stabilize, we typically need to apply a backward voltage and we can see a stable behavior in the LRS during the backward sweep of Figure 4 (a), below 9 V. If the voltage is now kept at low values (or 0V), the device stays in a LRS.

To get back to a high-resistance-state (HRS), a process similar to electroforming is used: a large forward voltage sweep is applied, until large conductance drops are observed (see black curve in Figure 4 (b)). We note that until the RESET (resistance increasing) process starts, the device behaves in exactly the same manner as it behaved at the end of the SET (resistance decreasing) process: the green and black curves are superimposed, highlighting the fact that the LRS is stable. We also note that the I-V curves in the LRS are non-linear. To achieve a stable, non-volatile HRS, the voltage must be stopped at high values (V_{RESET} in Figure 4 (b)).

It is found that the data in the LRS are best-fitted by a Poole-Frenkel model of conduction:^{16, 17}

Figure 4. Electrical switching process. (a) I-V characteristic curves showing the SET process. First, the voltage is increased and the current is found to increase non-linearly (black curve). Then, a backward voltage sweep is applied during which a permanent resistance change is achieved (green curve). The current ratio between the HRS and the LRS is found to equal 2.10^6 . (b) Typical voltage sweep cycling during which the device starts in a HRS (green curve, high voltages), then is SET (at ≈ 7 V) back to a LRS, and finally returns to the HRS (black curve, first significant conductance drop at ≈ 9 V). The red dashed curve is a fit of the data to the Poole-Frenkel model.

$$j = e\mu N_C E \exp \left[\frac{-e(\phi_T - \sqrt{qE/\pi\epsilon_i\epsilon_0})}{kT} \right] \quad (2)$$

where e is the electron charge, μ is the electronic mobility, N_C is the density of states in the conduction band, E the electric field, ϕ_T the trap energy level, ϵ_i and ϵ_0 the material and vacuum permittivities (respectively), k is the Boltzmann constant and T is the absolute temperature.

Poole-Frenkel conduction is a conduction mode common in dielectrics, whereby charge carriers are trapped by defects. It has been reported as a common conduction mode in amorphous carbons.^{18,19} As temperatures have increased enough to induce sublimation of the graphene at the location of the crack, it is reasonable to assume that temperatures were high enough to induce significant degradations to the graphene around the crack. These degradations might be responsible of this Poole-Frenkel behavior in the LRS.

By studying the switching process with voltage sweeps, we are able to define arbitrary values for the SET process (V_{SET}), the RESET process (V_{RESET}) and the reading process (V_{read}) (see Figure 4 (b) below the x-axis). By using these arbitrary values, it is possible to switch devices by using voltage pulses rather than sweeps (Figure 5). Figure 5 shows that R_{HRS}/R_{LRS} ratio values as high as 10^4 can be achieved for more than 100 cycles.

3.4 Electro-mechanical model

It is not the first time a graphene-based two-terminal memory is demonstrated.^{6,7} Although no direct observation has yet been reported, two different mechanisms are typically proposed for the switching.

The first one relies on the SiO_2 substrate. Because degradations to the substrate are observed during electroforming,⁷ it is believed that the oxygen may locally be moved aside, creating conductive SiO_{2-x} filaments. It is a very similar mechanism to that occurring in redox memories,²⁰ where reduced filaments are formed in a metal oxide due to the electric field (the oxygen is more electronegative hence tends to be repelled by positive charges). Redox memories are bipolar because if a negative charge is needed to SET (repel oxygen) the device, a positive charge will be needed to RESET (attract oxygen) it. In the case of the memories hereby demonstrated,

Figure 5. Endurance test showing the alternative resistance states (HRS and LRS) achieved during pulse cycling with a R_{HRS}/R_{LRS} ratio value of $\approx 10^4$. $V_{read} = 1V$, 10 ms. Between two read pulses, we apply either a SET pulse ($V_{SET} = 7V$, 1 s) or a RESET pulse ($V_{RESET} = 25V$, 10 ms)

the functioning is unipolar, which means that the direction of the electric field does not have an impact on the device functioning. Hence, if our memories are SET by the formation of Si filaments in the substrate, there is no driving force for them to be RESET through the application of an electric field of the same polarity. Consequently, we suggest that our memories do not function through the dielectric breakdown of the substrate.

The second proposed mechanism is based on the formation of graphitic filaments bridging the nano-gap.⁶ We believe this model to be convincing; nevertheless, it does not apply quantitatively to our memory devices, because we sometimes find conduction levels (after SET) very close to those of pristine devices, suggesting large contact areas. But devices demonstrated in other references⁶ are fabricated by electron-beam lithography and are much smaller than our devices. Hence, instead of atomic chains bridging the nano-gap, we suggest that stripes of graphene are effectively contacting both sides of the nano-gap. But for this bridging process to occur repeatedly, there must be a strong driving force that is controllable electrically.

In 2000, Rueckes et al.²¹ demonstrated a performant carbon nanotube-based non-volatile memory where the driving force for switching is entirely electro-mechanical. In the OFF state, their device is made of two nanotubes separated by an air gap of a few nm. Reading is done by applying a low electric field between these two nanotubes and measuring the current, which is limited by air tunneling. Switching to the ON state is done by applying a higher electric field, resulting in increasing attractive electrostatic forces due to the accumulation of opposed charges in the nanotubes at each side of the air gap. To get the nanotubes to bend and contact, these electrostatic forces have to overcome the mechanical forces opposing their bending. It was shown to be possible for certain conditions. Stability in the ON state was also found to be possible via the creation of van der Waals bonds between the two nanotubes. To get back to the OFF state, it was sufficient to apply a repulsive electric field, hence overcoming the van der Waals forces.

We propose that a similar mechanism is at stake here. In the OFF state, the flowing current is limited by tunneling. For higher electric fields, an electrostatic force builds up until it is large enough to overcome elastic and friction forces. It has already been shown that graphene can stretch and slide above SiO_2 when a mechanical force is applied to it.²² Then, as a contact is made between the two graphene sides, the electrostatic forces decrease as current starts flowing, resulting in the elastic forces taking over and pulling the two sides apart. As long as the electrical field is maintained, this process repeats itself, leading to rising temperatures through the Joule effect. When temperatures are high enough, covalent bonds form between the two graphene flakes, enabling stability in the ON state. The device is now in its LRS. To get back to the HRS, we have seen that a

similar process as electroforming may be used. Indeed, temperatures must rise high enough so that the covalent bonds insuring stability in the LRS are broken: then, the elastic forces take over, re-establishing the nano-gap.

4. CONCLUSION

We demonstrated a two-terminal graphene switch that can reversibly change its electrical resistance in a non-volatile manner with resistance ratio values of up to 10^6 . To get into a switchable state, a nano-gap must be created that effectively impedes the current flow. This nano-gap is formed by applying large electric fields to the pristine devices, resulting in heat generation by the Joule effect, followed by the formation and propagation of a crack. Then, this gap can be reversibly closed via attractive electrostatic forces created when a large electric field is applied to the opened device. For the device to be stable (non-volatile) in the hence achieved "closed" state, covalent bonds must form to overcome the graphene recoil forces. This occurs when the two sides are in contact and high temperatures are generated by the electrical current (at V_{SET}). To re-open the gap, a higher voltage (V_{RESET}) is applied so that the Joule effect breaks the covalent bonds. To the best of our knowledge, this device is effectively the first demonstrated graphene-based planar electro-mechanical switch.

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