Nonvolatile resistive switching in graphene oxide thin films

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Reliable and reproducible resistive switching behaviors were observed in graphene oxide (GO) thin films prepared by the vacuum filtration method. The Cu/GO/Pt structure showed an on/off ratio of about 20, a retention time of more than 10^4 s, and switching threshold voltages of less than 1 V. The switching effect could be understood by considering the desorption/absorption of oxygen-related groups on the GO sheets as well as the diffusion of the top electrodes. Our experiments indicate that GO is potentially useful for future nonvolatile memory applications. © *2009 American Institute of Physics*. [doi:10.1063/1.3271177]

Resistive random access memory (RRAM), which is based on resistance switching induced by external electrical stimulations, has attracted great attention for its potential applications in next generation nonvolatile memory due to its simple structure, nondestructive readout, high operation speed, long retention time, and low power consumption. The resistive switching effect has been observed in a variety of materials, including perovskite oxide materials [such as $Pr_{1-x}Ca_xMnO_3$ (Ref. 1) and Cr-doped $SrZrO_3$ (Ref. 2)], binary transition metal oxides [such as NiO,[3] ZnO,[4] and ZrO_2 (Ref. 5)], chalcogenides,[6] organic materials,[7] and amorphous silicon.[8] In last decades, carbon-based materials have been studied intensively as a potential candidate to overcome the scientific and technological limitations of traditional semiconductor devices.[9–11] It is worthy mentioning that most of the work on carbon-based electronic devices has been focused on field-effect transistors.[12,13] Thus, it would be of great interest if nonvolatile memory can also be realized in carbon so that logic and memory devices can be integrated on a same carbon-based platform. Herein, we report resistive switching behaviors in a Cu/graphene oxide (GO)/Pt sandwiched structure. Reversible bipolar resistive switching behaviors were observed. The possible physical mechanism of the switching effect is discussed.

GO with an ultrathin thickness is attractive due to its unique physical-chemical properties. GO can be readily obtained through oxidizing graphite in mixtures of strong oxidants, followed by an exfoliation process. Due to its water solubility, GO can be transferred onto any substrates uniformly using simple methods such as drop-casting, spin coating, Langmuir–Blodgett deposition and vacuum filtration. The as-deposited GO thin films can be further processed into functional devices using standard lithography processes without degrading the film properties.[14,15] In this work, GO thin films of ~30 nm in thickness were prepared at room temperature (RT) by the vacuum filtration method. First we obtained GO suspensions through the soft-chemical delamination of GOs as described in Ref. 16. Then 50 g of GO suspension with a concentration of 6 mg/L was filtered through a cellulose ester membrane to achieve uniform GO thin films. The film thickness could be well controlled by tuning the GO concentration or filtration volume. The as-filtered GO flakes were then transferred from the filter membrane onto commercial $Pt/Ti/SiO_2/Si$ substrates. The thickness of GO flakes was typically controlled in the range of 20–40 nm. In order to measure the electrical properties, Cu top electrodes with a thickness of 200 nm and diameter of 100 μm were deposited at RT by electron beam evaporation with an *in situ* metal shadow mask. The *I-V* characteristics of Cu/GO/Pt structures were measured at RT by Keithley 4200 semiconductor characterization system with voltage sweeping mode. During the measurement, a bias voltage was applied between the top (Cu) and bottom (Pt) electrodes with the latter being grounded. The schematic structure of the sandwiched devices is depicted in Fig. 1(a).

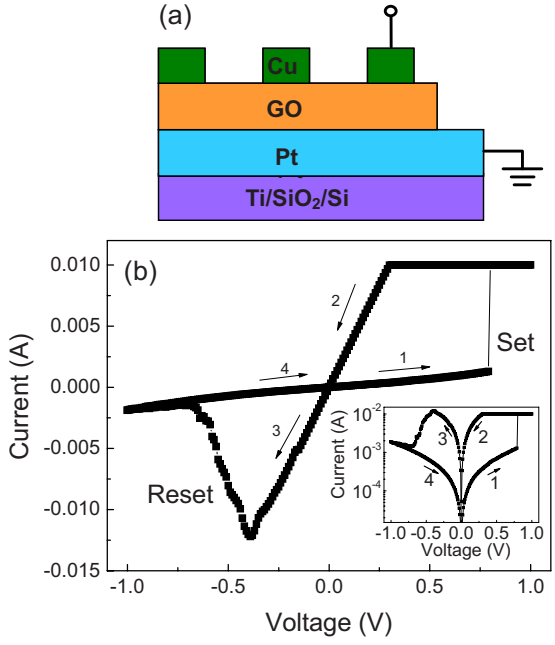

FIG. 1. (Color online) (a) A schematic configuration of the Cu/GO/Pt sandwiched structure. (b) *I-V* characteristics of the Cu/GO/Pt structure. The arrows indicate the sweep direction. The inset shows the *I-V* characteristics in semilogarithmic scale.

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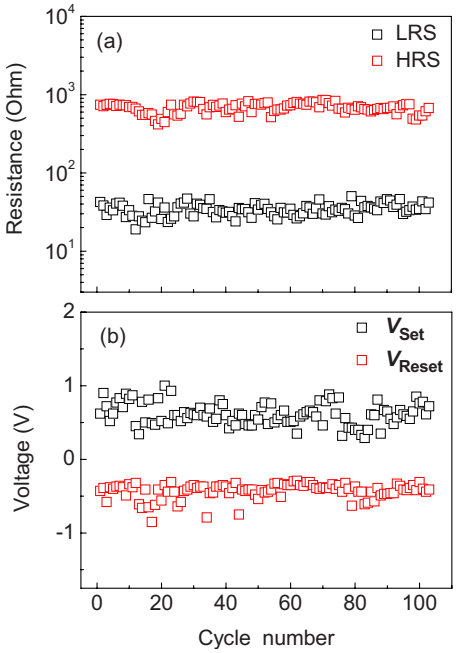

FIG. 2. (Color online) (a) The endurance performance, and (b) the distributions of the programming voltages (V_{Set} and V_{Reset}) of the Cu/GO/Pt memory cell.

Figure 1(b) plots a typical *I-V* curve of a Cu/GO/Pt cell. The inset of Fig. 1(b) shows the same *I-V* curve in a semilogarithmic scale. During the measurement, the voltage was swept in a sequence of $0\ V \rightarrow 1\ V \rightarrow 0\ V \rightarrow -1\ V \rightarrow 0\ V$ at a rate of 0.01 V/s. No forming process was necessary for activating the resistive switching effect. While increasing the positive voltage steadily, the current jumps abruptly at a voltage value of about 0.8 V. The device switches from the high resistance state (HRS or off state) to a low resistance state (LRS or on state), which is called the "Set" process. A current compliance (10 mA in this work) is usually needed during the Set process to prevent the sample from a permanent breakdown. By sweeping the voltage from 1 to −0.4 V, the device holds on the LRS, and starts switching from the LRS to the HRS ("Reset" process) from −0.4 V. At the voltage of −0.75 V, the cell recovers to the HRS, and holds until next Set process. The *I-V* characteristics exhibit a typical bipolar switching behavior. The device yield of the Cu/GO/Pt structure is more than 50%.

In order to investigate the endurance performance of the Cu/GO/Pt memory device, cyclic switching operations were conducted. Figure 2(a) shows the evolution of resistance of the two well-resolved states in 100 cycles. The resistance values were read out at −0.1 V in each dc sweep. Although the resistance values of both HRS and LRS show some fluctuations, the on/off ratios are about 20 without any obvious degradation within 100 cycles. The distribution of the programming voltages (V_{Set} and V_{Reset}), another critical parameter to evaluate the memory device, is shown in Fig. 2(b). V_{Set} and V_{Reset} distribute in a range of 0.3 to 1 V and −0.3 to −0.9 V, respectively. The switching threshold voltages of the Cu/GO/Pt sandwiched structure are lower than those of most reported RRAM devices.[1,3,4,8,17]

The retention performance of the memory cell at RT is shown in Fig. 3. The device was switched on or off by dc voltage sweeping. Then the resistance of LRS or HRS was read out at a reading voltage of 0.1 V. The readout was found

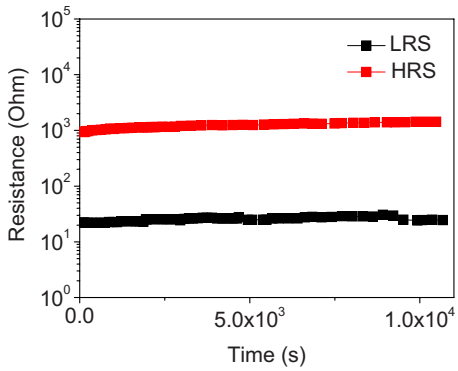

FIG. 3. (Color online) Retention for the LRS and HRS of the Cu/GO/Pt device at RT.

to be nondestructive. Both the LRS and HRS resistances can be retained for more than 10^4 s without an external electrical power, indicating that the memory device is nonvolatile and stable at RT.

We intend to attribute the observed resistive switching to the desorption/absorption of oxygen-related groups on the GO sheets as well as the diffusion of the top electrodes. As is well known, a GO layer can be considered as a graphene sheet with epoxide, hydroxyl, and/or carboxyl groups attached to both sides, and physical properties of GO can be modulated by those chemical functionalities on the surface.[18,19] We propose that the desorption and absorption of epoxide, hydroxyl, and carboxyl groups near the Cu top electrode may be responsible for the observed resistive switching in the Cu/GO/Pt cell.[20,21] When there are an amount of epoxide, hydroxyl, and carboxyl groups on the GO surface, the conductance of the Cu/GO/Pt cell is assumed to be low due to sp^3 bonding feature. As a positive bias is applied on the top electrode, oxygen-related functional groups inside the GO layer(s) close to the Cu top electrode are removed, resulting in an amount of sp^2 bonds. The conductance of the device becomes higher due to an increase in the concentration of interlayer π electrons. As a result, the device is switched to the LRS. While sweeping the voltage to certain negative values, the oxygen-related groups diffuse toward GO sheets and attach to them again. Correspondingly, the memory cell returns to the HRS. Therefore, the desorption and absorption of the oxygen-related groups on the GO sheets correspond to the on and off states, respectively. In addition, various metals (such as Ag, Au, and Ti) as top electrodes were deposited on GO films and the *I-V* characteristics were investigated. The resistive switching behaviors were also observed. The devices with Cu top electrodes showed larger on/off ratio and higher device yield compared to those with Au top electrodes. This suggests that the formation/rupture of metal filaments in the GO film due to the diffusion of top electrodes under an external voltage may be responsible for the switching as well besides the desorption/adsorption of oxygen-related groups. Of course, in order to clarify the real origin of the observed resistive switching behaviors, more investigations are needed.

In summary, GO thin films were prepared on $Pt/Ti/SiO_2/Si$ substrates by vacuum filtration method. Reliable and reproducible resistance switching behaviors were found in the Cu/GO/Pt devices. The resistance ratio between HRS and LRS is about 20. The memory devices exhibited good retention characteristics and low switching voltages.

The observed switching effect might originate from the desorption/absorption process of oxygen-related groups on the GO sheets and also the diffusion of the top electrodes.

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