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Effects of Graphene Oxide Layer on Resistive Memory Properties of Cu/GO/SiO_2/Pt Structure

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A Cu/graphene oxide (GO)/SiO_2/Pt structure was synthesized in order to investigate the effects of the GO layer on the properties of resistive memory. The resistance of the Cu/GO/SiO_2/Pt structure can be reversibly switched between a high-resistance state and a low-resistance state by dc voltages with different polarities. Such resistance switching is dominated by the electrochemical reaction with Cu conducting filaments. The folded and layered structure of the GO film was found to limit the number of available pathways for Cu ion migration, resulting in the formation of fewer Cu conducting filaments in the SiO_2 layer. Hence, the GO layer improved the stability of resistance switching. The synthesized Cu/GO/SiO_2/Pt structure demonstrated low operating voltages, a low operating power, a high resistance ratio, and good reliability, which makes it suitable for use as a next-generation nonvolatile memory structure.

1. Introduction

Graphene has recently been a material of much interest owing to its high thermal conductivity, high electrical conductivity, and high flexibility.(1) Some difficulty remains, however, in the fabrication of a low-price and large-area graphene layer. In attempts to find a resolution to this issue, graphene oxide (GO) has been fabricated by chemical methods and then the synthesized GO has been reduced to graphene in many studies.(2) GO exhibits the properties of an insulator while remaining both flexible and transparent. The electronic and optical properties of GO can be tuned by modifying the extent of film oxidation. GO can therefore be investigated for many applications.(3) So far, many graphene-related materials for sensor applications have been proposed. Wang *et al.* used GO nanostructures for hydrogen gas sensing.(4) Ang *et al.* fabricated a solution-gate field effect transistor on few-layer graphene as a pH sensor.(5) Bae *et al.* used chemical vapor deposition (CVD)-grown graphene to fabricate a transparent and stretchable strain sensor.(6)

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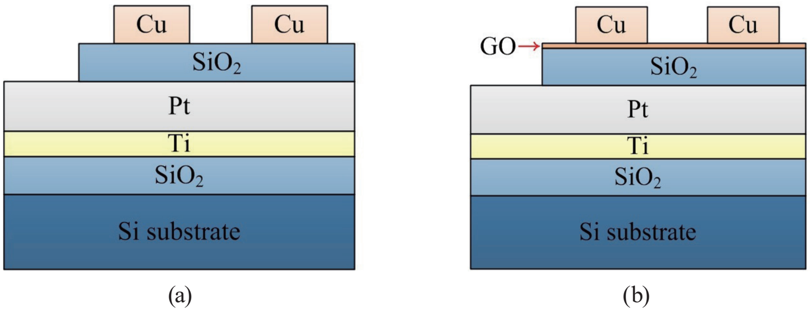
Nowadays, flash memory is one of the most commonly used types of nonvolatile memory (NVM). In the near future, however, it will suffer serious reliability issues owing to its physical limitations related to continuous scaling. Alternative devices such as magnetoresistive random-access memory (MRAM),(7) ovonic unified memory (OUM),(8) and resistive random access memory (RRAM)(9) are therefore garnering a great deal of attention. Among these devices, RRAM, with a simple metal/insulator/metal structure, has the ability of reversible resistive switching and is therefore attracting much interest for use in next-generation NVM applications. Several materials such as SiO_2,(10) NiO,(11) HfO_2,(12) and GO,(13) have been proposed for use in RRAMs, as each demonstrate a resistive switching behavior with a different switching mechanism. In general, the resistive switching mechanisms can be classified as the valence change effect,(14) thermochemical reaction,(11) and electrochemical reaction.(10) Although the conventional Cu/SiO_2/Pt structure has been investigated for use as an electrochemical RRAM device,(10) it demonstrated a large switching variation, resulting in operation failure during successive switching cycles,(15) further complicating the circuit design of memory applications.

In this study, a GO film was used as an insert layer to facilitate the fabrication of a Cu/GO/SiO_2/Pt structure. The insertion of the GO layer improved the stability of resistive switching owing to the folded and layered structure of the GO layer. This structure serves to limit the number of available pathways for Cu diffusion from the Cu electrode into the SiO_2 layer, resulting in fewer formation sites and therefore a more stable reversible switching.(16)

2. Experimental Procedure

A 20 nm SiO_2 layer was deposited on a Pt-coated (Pt/Ti/SiO_2/Si) substrate by radio-frequency magnetron sputtering at room temperature. A thermal evaporator then deposited a 200 nm Cu layer in order to form the Cu/SiO_2/Pt structure (control sample). The device area patterned by a shadow mask is 5×10^{-5} cm^2. The GO water solution was prepared by the modified Hummer's method.(17) To investigate the effect of a GO layer, a 5 nm GO layer was deposited by spin coating a water solution of GO onto the SiO_2 layer. Following that, a 200 nm Cu layer was deposited to form the Cu/GO/SiO_2/Pt structure (GO sample). Illustrations of these two structures are shown in Fig. 1. A transmission electron microscopy device (TEM,



(a) (b)

Fig. 1. (Color online) Schematic diagrams of the (a) control and (b) GO samples.

JEM-2010) was used to observe the thickness and microstructure of the GO sample. Electrical measurements were performed by an Agilent E5250A low-leakage switch mainframe and an HP 4155B semiconductor parameter analyzer at room temperature in air. The voltage signal was applied to the Cu top electrode, while the Pt bottom electrode was grounded.

3. Results and Discussion

Figure 2 shows a cross-sectional TEM image of the Cu/GO/SiO_2/Pt structure. The GO layer is only 5 nm in thickness and can be seen to have a folded, layered structure. The GO layer was obtained by oxidizing graphite using strong oxidants and an exfoliation process.(17) The GO film deposited via spin coating with a GO water solution therefore demonstrates uniformity.

Figure 3 shows the resistive switching behaviors of the two samples. The resistance of the control sample can be switched from the initial-resistance state (IRS) to a low-resistance state (LRS) by inducing a positive voltage (forming voltage), the process of which is known as the forming process. The resistance can then be switched from the LRS to a high-resistance state

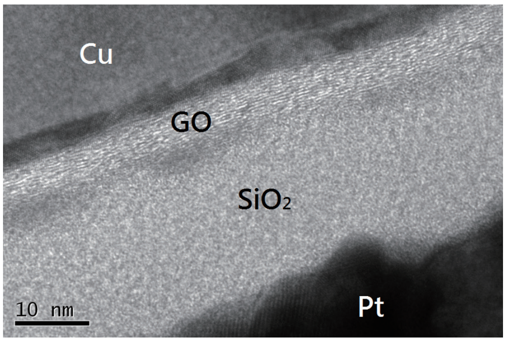
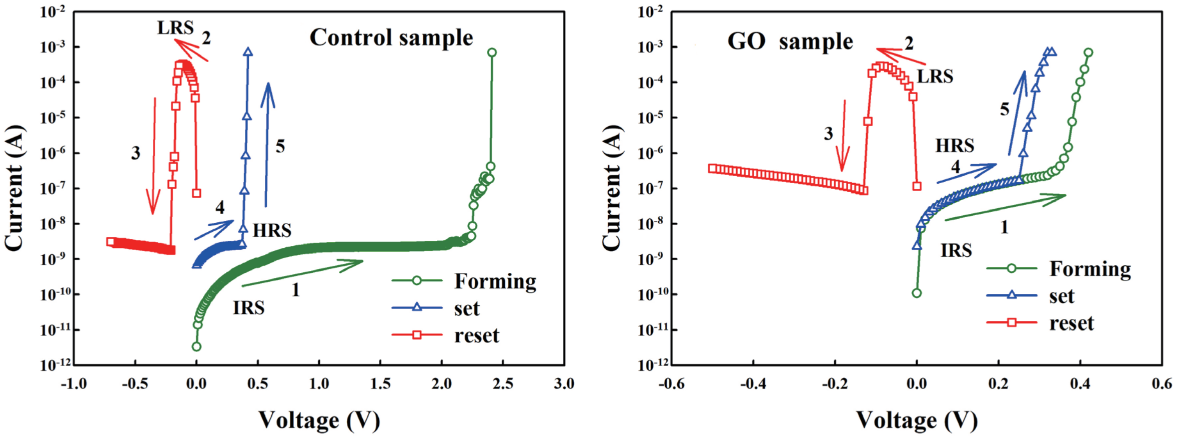


Fig. 2. Cross-sectional TEM image of the Cu/GO/SiO_2/Pt structure.



(a) (b)

Fig. 3. (Color online) Resistive switching behaviors of the (a) control and (b) GO samples in air.

(HRS) by inducing a negative voltage (reset voltage), the process of which is known as the reset process. After that, the resistance can then be switched to the LRS by inducing a positive voltage (set voltage), which is known as the set process. Finally, the resistance of the control sample can be reversibly switched using the set voltage (V_{set}) and reset voltage (V_{reset}). To prevent permanent damage, a current compliance of 700 μA was used during the forming and set processes. The switching behavior of the GO sample was found to be similar to that of the control sample; the operating voltages of the GO sample, however, are lower than those of the control sample. The switching mechanism proved to be a very important characteristic of the RRAM device. The material group, device structure, and interface status have all been known to affect the switching mechanism.(18) From the device structure, bipolar switching behavior, and positive temperature coefficient of LRS resistance (not shown), the switching mechanism of the Cu/SiO_2/Pt structure was determined to be dominated by the Cu conducting filaments of the electrochemical reaction. When a positive voltage is applied to the sample, Cu ions are ionized from the Cu electrode and become dissoluted into the SiO_2 layer. Cu conducting filaments then grow from the Pt electrode toward the Cu electrode, and the resistance then becomes an LRS. Following this phenomenon, when a negative voltage is applied to the sample, the reset process is induced, which consists of the Joule-heating-assisted oxidation of Cu atoms at the thinnest part of the metal filament, leading to the rupture of the conducting filaments. The reversible resistive switching occurs as a result of the formation and rupture of Cu conducting filaments. The GO sample using a Cu electrode demonstrated a similar bipolar switching behavior. As shown in Fig. 4, the temperature coefficient of the LRS resistance of the GO sample is 4.02×10^{-3} K^{-1}, which is close to that of bulk copper. It can therefore be deduced that the conducting filaments of this sample are composed of copper, meaning that the switching mechanism of the GO sample is due to the formation and rupture of Cu conducting filaments, as described previously. Hong *et al.* proposed that the resistive switching mechanism of the Al/GO/metal memory is governed by oxygen migration and Al diffusion.(19) Since the switching mechanisms of the two samples were found to be the same, it can be said that the oxygen-related groups within the GO layer do not strongly affect the resistive switching.

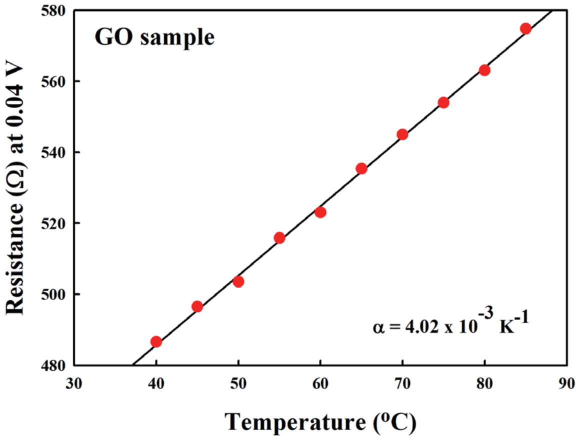
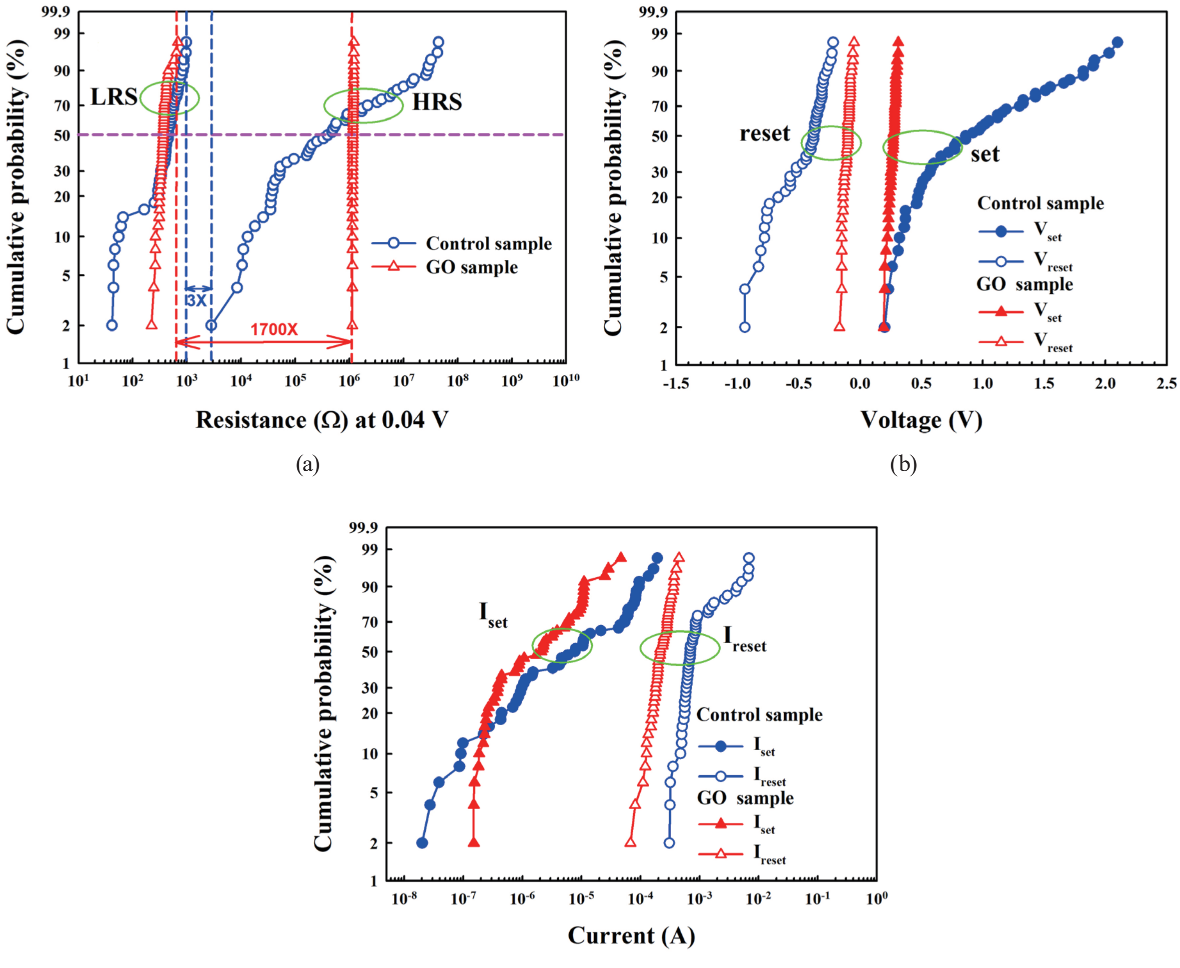


Fig. 4. (Color online) Temperature coefficient of LRS resistance of the GO sample.

Figure 5(a) shows the cumulative probabilities of the HRS and LRS resistances of the two samples. The LRS and HRS resistances of the control sample show large variations, indicating that an unstable resistive switching occurred in the control sample. However, the switching variations of the LRS and HRS resistances of the GO sample are shown to be relatively small, indicating that the GO sample underwent a very stable resistive switching. The two samples had almost the same median value of LRS resistance, which is a result of both samples having the same current compliance during the set process.(20) The GO sample demonstrated a higher HRS resistance than the control sample, owing to the thicker GO/SiO_2 stacked structure and fewer residual filaments in the SiO_2 layer. Owing to the extremely large switching variation, the magnitude of the switching margin of the control sample is only 5 times. In contrast, the GO sample has a large switching margin of 1700 times. Figure 5(b) depicts the cumulative probabilities of the V_{set} and V_{reset} of the two samples. The control sample demonstrated larger median values of the operating voltages than the GO sample. In addition, the control sample



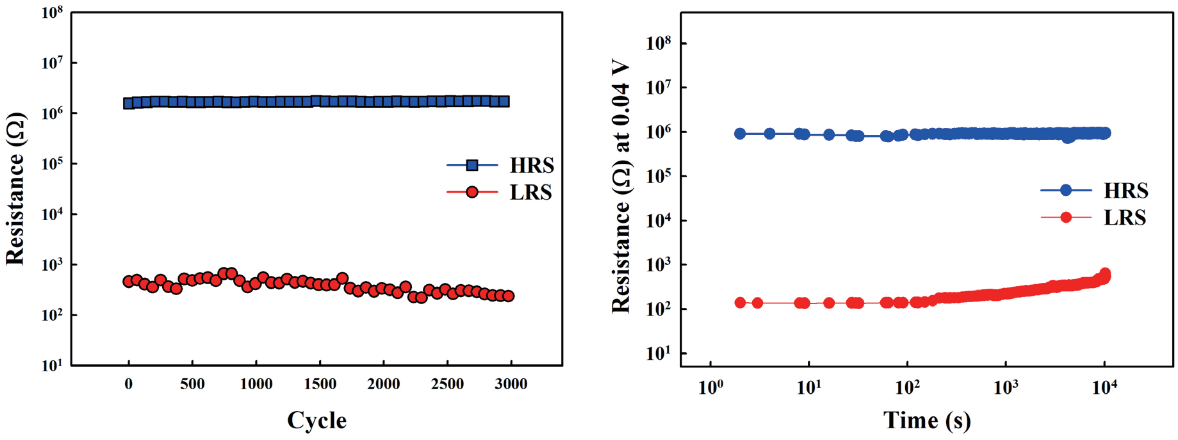
(a) (b)

(c)

Fig. 5. (Color online) Switching parameters of the two samples: (a) LRS and HRS resistances, (b) set and reset voltages, and (c) set and reset currents.

showed a much larger switching variation than the GO sample. Song *et al.* proposed the use of an AlO_x/WO_x bilayer in order to stabilize the resistive switching and reduce the reset current.(21) In this study, the WO_x layer demonstrated the ability to control the number of conductive filaments created and therefore reduce the reset current by more than one order when compared with that of the single-layer structure. The formed conducting filaments may lead to a template effect on the proceeding resistive switching cycles.(16) Fewer conducting filaments can therefore stabilize the resistive switching. Because the GO film was deposited by spin coating with a GO water solution, the resulting GO layer would be of a folded and layered structure. This folded and layered structure of the GO layer would therefore serve to limit the number of diffusion pathways from the Cu electrode to the SiO_2 layer in the GO sample, resulting in the observed stable reversible switching.(16) As fewer pathways form during the resistive switching in this case, lower operating voltages and currents are required to form and rupture Cu conducting filaments. The GO sample therefore not only has lower reset and set currents than the control sample; it also has reduced operating voltages and currents, resulting in decreased power consumption.

The control sample may only be reversibly switched for about 1000 cycles. However, owing to the unstable switching demonstrated by this sample, the switching margin was found to be very small. Figure 6(a) shows the endurance characteristics of the GO sample. This sample was shown to endure reversible switching for more than 3000 stable cycles, and the switching margin was found to be more than 10^3. Figure 6(b) shows that the retention time of the GO sample was more than 10^4 s at room temperature, demonstrating the nonvolatility of the GO sample. The GO sample therefore has superior memory reliability and is suitable for use as a next-generation NVM.



(a) (b)

Fig. 6. (Color online) (a) Endurance characteristics of the GO sample. (b) Retention characteristics of the GO sample.

4. Conclusion

A Cu/GO/SiO_2/Pt structure was synthesized in order to investigate the effect of a GO layer on the resistive switching property of this structure. The layer-structure GO film was found to limit the number of diffusion pathways available for the Cu ions as they migrate from the Cu electrode to the SiO_2 layer. Hence, fewer conducting pathways were formed and an improvement in the stability of resistive switching was observed because of this. The GO sample was also observed to have lower operating voltages and currents. The sample endured more than 3000 switching cycles and the retention time was greater than 10^4 s at room temperature. The GO sample demonstrated a stable resistive switching and good reliability, therefore making it suitable for use in a next-generation NVM device.

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