Flexible Resistive Switching Memory Device Based on Graphene Oxide

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***Abstract*—A resistive switching memory device based on graphene oxide (GO) is presented. It is found that the resistive switching characteristic has a strong dependence on electrode material and GO thickness. In our experiment, an Al/GO/ITO structure with 30-nm-thick GO shows good switching performance with an on/off resistance ratio of 10^3, low set/reset voltage, and excellent data retention. The GO memory is also fabricated on a flexible substrate with no degradation in switching property, even when the substrate is bent down to 4-mm radius, indicating that the GO memory is an excellent candidate to be a memory device for future flexible electronics.**

***Index Terms*—Flexible memory, graphene oxide, resistive switching memory.**

I. Introduction

RESISTIVE switching random access memory (ReRAM) has attracted attention because of its potential for high-speed and low-voltage operation, high packing density, and structural simplicity. Many research groups have explored organic and inorganic materials to fabricate resistive switching elements for memory operation [1], [2]. However, research on ReRAM is still in an early stage compared to other memories in production. On the other hand, flexible electronics are becoming more popular than ever. Most flexible electronic devices are currently based on organic materials, and their performance is still far inferior to that of nonflexible inorganic devices. Very recently, a letter reported that graphene oxide could show resistive switching characteristics and attributed this switching to the desorption/absorption process of oxygen-related groups and the diffusion of the top electrode [3]. In this letter, we also report a resistive switching memory device based on a graphene oxide layer prepared using different electrodes and a fabrication method, demonstrating lower operation voltage and improved on/off current ratio. The dependence of the device structure on switching performance and the flexible characteristics of the graphene oxide memory device are also presented.

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II. Device Fabrication

The resistive switching memory device was fabricated as a metal–insulator–metal (MIM) capacitor structure, where graphene oxide was used as the insulator layer of the capacitor. Soda–lime glass coated with indium thin oxide (ITO) or aluminum was used as a starting substrate. After wet chemical cleaning using acetone and methanol, followed by DI water rinse, the sample was exposed to UV light to enhance the adhesion of graphene oxide to the bottom metal electrode. Then, the graphene oxide layer was spin coated on the bottom electrode using a solution containing graphene oxide particles, H_2O, and methanol. A N_2 blow to the wafer surface was done during spin coating to enhance the desorption of methanol and improve the uniformity of the graphene oxide thickness [4]. A spin-coating process of graphene oxide with a spin speed of 1000 r/min provided a 3-nm-thick graphene oxide layer on the electrode in our experiment. For thicker graphene oxide layer formation, the spin coating was repeated until the targeted thickness was achieved. All samples were annealed at 100 °C for 1 h for better crystallinity and uniformity after the deposition of graphene oxide. An aluminum or gold top electrode with a diameter of 180 μm was then deposited by thermal evaporation of the metal through a shadow mask. Three different combinations of electrodes (Al/GO/ITO, Al/GO/Al, and Au/GO/ITO) were used to investigate the effect of electrode material dependence, and three different GO thicknesses (15, 30, and 45 nm) in the Al/GO/ITO structure were also used. To investigate the flexible characteristics of GO switching memory, the MIM structure was fabricated on a polyethylene terephthalate (PET) substrate. For the flexible device, the bottom and top electrodes were ITO and Al, respectively.

III. Results and Discussion

The I–V characteristics of MIM devices with 30-nm-thick GO and three different combinations of electrodes (Al/GO/ITO, Al/GO/Al, and Au/GO/ITO) are shown in Fig. 1. The inset of the figure shows the image of the GO surface measured by an atomic force microscope (AFM). The root-mean-square (rms) roughness of the 30-nm-thick GO was 4.68 nm. The same as in other ReRAM devices, a forming process was necessary in GO switching memory. For the forming process, a strong positive bias to the top electrode from 0 to 5 V was applied to the device, which caused the current to fluctuate in a low resistive state and then turned the device into a high resistive state. However, the initial state of the GO ReRAM was not always in a low resistive state. Some virgin samples showed a high resistive state. In any cases, the forming process was necessary for the subsequent stable switching operation. In switching property measurement, a negative-voltage sweep was first done up to -5 V and returned to 0 V, followed by a positive-voltage sweep to $+5$ V and then returned to 0 V. It should be noted that Au and ITO have a high work function of $\sim$5 eV, while Al has a low work function of $\sim$4.2 eV. The work function of ITO can vary, depending on the deposition process and the postdeposition annealing condition [5], [6]. In our experiment, ITO was deposited by e-beam evaporation, followed by post-deposition annealing in air ambient at 400 °C. In this case, the work function of ITO is around 5 eV [5]. Interestingly, in our experiments using Al/GO/Al and Au/GO/ITO samples, where both electrodes had the same work-function values, switching characteristics were not observed. The resistive switching from high-resistance state (HRS) to low-resistance state (LRS) or vice versa was observed only in the Al/GO/ITO structure where the bottom and top electrodes had a different work function. Such a tendency was confirmed again in our further experiments by testing other two structures—Au/GO/Pt and Al/GO/Pt. In our experiment, the Au/GO/Pt structure did not show switching characteristics, while the Al/GO/Pt structure did show. However, in [3], the Au/GO/Pt structure did show switching characteristics, although the performance was not as good as ours. Such an inconsistency probably originated from the use of different solutions in the preparation of GO. This indicates that not only the electrode work function but also the process-induced material variation could affect the switching behavior. Such a tendency was observed regardless of GO thickness. In our separate study, it is found that the distribution of oxygen groups (C = O and Al–O bondings) is modified by the applied voltage, and thus, the switching mechanism is believed to be related to the movement of oxygen in GO. As this letter is aiming for a rapid report of the new findings, the detailed mechanism study will be submitted to other full-length journals in the near future. In the case of Al/GO/ITO, the on/off current ratio had a stable value of $\sim 10^3$, as shown in Fig. 1. This result is 50 times better than the first report, which had an on/off current ratio of only 20. As only the Al/GO/ITO structure showed resistive switching characteristics in our experiment, all the further investigations of GO memory were done on the Al/GO/ITO structure.

Fig. 2 shows the GO thickness dependence on memory characteristics, such as ON/OFF-state resistance, set/reset-voltage variations, and switching operation probability. A 100% probability of switching operation means that all the devices measured show a clear switching behavior. In this measurement, 30 measurements were done for each GO thickness. It is important to note that the 100% operation of resistive switching was observed only at a certain thickness range of GO, as shown in Fig. 2(c). As some samples with GO thicknesses of 15 and 45 nm did not show switching characteristics, the data of resistance and voltage variations in Fig. 2(a) and (b) were obtained from samples that showed clear switching characteristics. The HRS/LRS ratios of 30- and 45-nm GO devices were

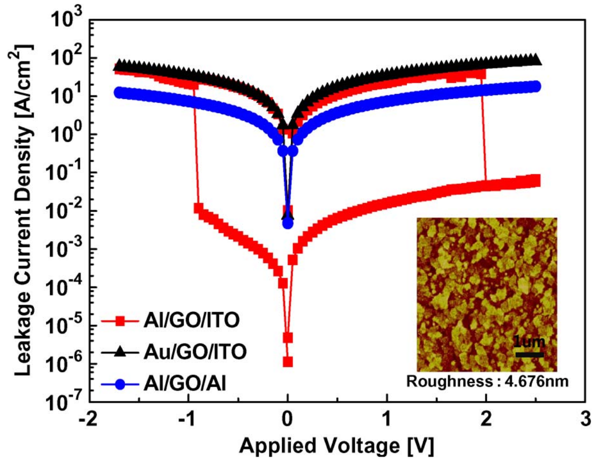

Fig. 1. Current–voltage characteristics of graphene oxide with different electrodes. Only the Al/GO/ITO structure shows resistive switching characteristics. The inset shows the AFM image of the 30-nm-thick GO layer. The measured area is 5×5 μm^2, and the rms roughness is 4.676 nm.

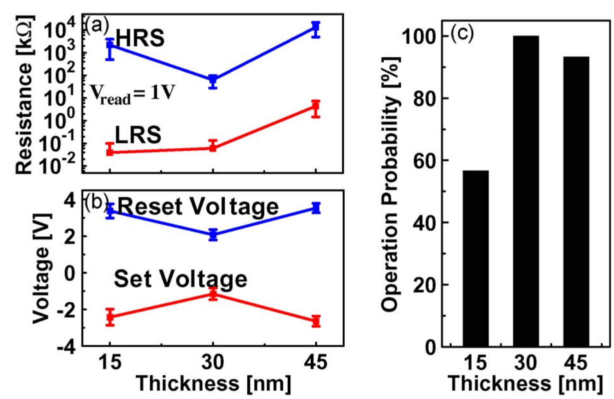

Fig. 2. (a) Resistance, (b) set/reset voltage, and (c) operation probability of GO memory devices with different GO thicknesses. The GO memory device has an Al/GO/ITO structure. The resistance was read at 1 V.

almost identical as 10^3, but the 30-nm GO sample showed lower resistance for both states and also had smaller sample-to-sample variation. The 30-nm GO sample had the lowest set/reset voltage among the three different thicknesses of the GO samples. More importantly, only the 30-nm GO sample showed 100% probability of switching characteristics. Based on the data shown in Fig. 2, it can be concluded that the thickness of 30 nm is an optimum investigated thickness in our experimental condition. It is believed that such an optimum thickness will vary, depending on other process parameters, such as GO solution density, graphene particle size, etc. The point in this result is to show that the performance of GO memory has a strong dependence on GO thickness.

The endurance and retention properties of the Al/GO/ITO structure with a 30-nm-thick GO layer are shown in Fig. 3. For the cycling measurement, ± 3 V was applied to the device. The resistance values of HRS and LRS were monitored at 1 V. During 100 switching cycles, the resistances of HRS and LRS maintained stability with a ratio of 10^3, and the resistance fluctuation was also quite small. The programming voltages (V_{Set} and V_{Reset}) were also almost constant as -1.6 and 2 V, respectively. The room-temperature retention data in Fig. 3(b) show no noticeable degradation up to 10^7 s.

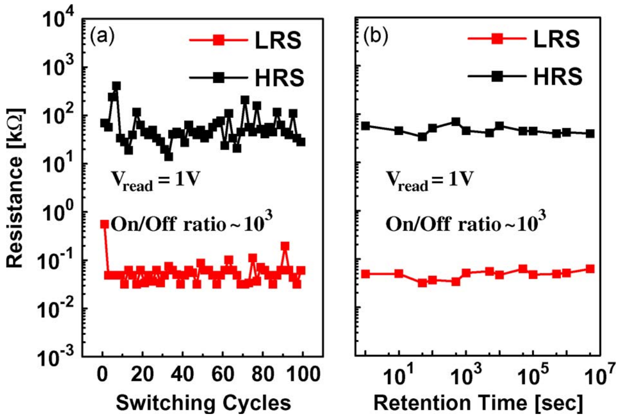

Fig. 3. (a) Endurance and (b) retention characteristics of GO memory devices with a 30-nm-thick GO layer.

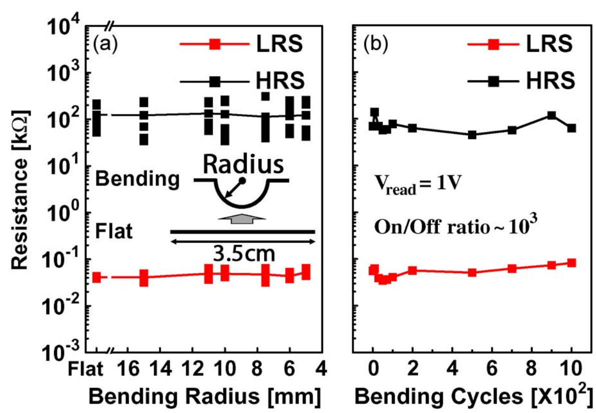

Fig. 4. (a) Resistance as a function of bending radius of the GO memory device fabricated on a flexible substrate. (b) Reliability of the flexible GO memory device. The memory device shows no degradation by bending down to 4-mm radius and 1000 times repeated bending. The resistance was read at 1 V.

The same structure of the GO memory device (Al/GO/ITO with a 30-nm-thick GO layer) was also fabricated on a PET substrate to evaluate the flexible characteristics of the GO memory device for future flexible electronic applications. In this letter, resistance was measured by direct probing on the bent sample. Six randomly selected devices were measured at a reading voltage of 1 V. In the flat state, the substrate was 35×35 mm^2. The substrate was bent to various bending radii, and the resistance variation as a function of bending radii is shown in Fig. 4(a). Surprisingly, no change in HRS/LRS resistance value and ratio was observed at the bending radius of down to 4 mm, indicating very high flexibility of the GO memory device. The reliability of the flexible GO memory device was also evaluated, and the result is shown in Fig. 4(b). The PET substrate with the GO memory device was repeatedly bent to 12-mm bending radius. The resistance of HRS/LRS shows no noticeable degradation up to 1000 times of repeated bending, demonstrating excellent reliability in flexibility.

IV. Conclusion

The characteristics of a resistive switching memory device based on graphene oxide have been investigated. It was found that there was an optimum thickness of GO to have 100% successful switching operation. The device exhibited good on/off resistance ratio, endurance, and retention, demonstrating that the resistive switching memory is another important application of graphene-based materials. It should be noted that the fabrication cost of a GO device can be much lower than that of other resistive switching memory devices that use metal oxides prepared by an atomic layer deposition or sputtering process. In addition, the excellent reliability of the flexible substrate indicates that the GO memory is a promising candidate for future flexible electronic applications.

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