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Impedance spectroscopy analysis of the switching mechanism of reduced graphene oxide resistive switching memory

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ABSTRACT

In this study, we investigated the resistive switching behavior of pristine graphene oxide and thermally reduced GO. Impedance spectroscopy and current–voltage analysis were used to verify the possible physical mechanism of the switching operation. Our observations demonstrated that, the switching operation originates from the oxidation/reduction at the top interface of Al electrode and oxygen migration inside the active layer. Reversible redox reaction $Al^{+1} + xO^{-2} \leftrightarrow AlO_x$ is ground for the conduction electrons.

1. Introduction

Recently, resistive random access memory (ReRAM) has attracted considerable attention and has been predicted to become the front runner of non-volatile memory due to its simple structure, high operation speed, good scalability, and multi-bit storage [1]. A large variety of materials exhibit resistive switching effects, including complex perovskite oxides, amorphous silicon, amorphous carbon, organic materials and binary transition metal oxides [2–6].

In 2004 by Novoselo et al. reported forming individual graphene sheet, which led to a deluge of international research. Ideally, graphene is a two-dimensional material with carbon atoms densely packed in a honeycomb lattice [7,8]. Graphene can be obtained by micro-mechanical exfoliation [9], chemical vapor deposition (CVD) epitaxy growth [10,11], and reduction of graphene oxide (GO) [7,12,13]. However, synthesizing a uniform, large piece of graphene film is still a challenge. Since graphene oxide, which consists of a single graphene layer bound to oxygen as carboxyl, hydroxyl, or epoxy groups, is water soluble, it can be uniformly deposited onto any substrate by simple methods, such as drop-casting, spin coating, Langmuir–Blodgett deposition and vacuum filtration. This characteristic graphene oxide is an advantage for large-scale, flexible, transparent and printable applications [14]. Furthermore, the band structure and electronic properties of graphene oxide can be modulated by changing the quantity of oxygen functionalities attached to the surface using a physical and chemical reduction process. Therefore, graphene oxide and reduced GO (*r*GO) are promising materials for microelectronic devices, such as ReRAM. Reports have identified reliable and reproducible resistive switching of graphene oxide [15–19], *r*GO thin film [20] and conjugated-polymer functionalized GO films [21]. However, the microscopic origin of resistive switching of thin graphene oxide and *r*GO films is not fully understood.

Impedance spectroscopy is an important tool for studying the charge carrier dynamics, the interfacial characteristics, and dielectric properties of device and equivalent circuit models [22]. In this study, we performed impedance measurements to study the switching behavior in both high-resistance state (HRS) and low-resistance state (LRS) of reduced graphene oxide based memory cells. The results provide more information for understanding the fundamental physics and switching mechanism of bipolar resistive switching in *r*GO memory devices.

2. Experiment details

Indium tin oxide (ITO), aluminum (Al) and gold (Au) was used as the bottom electrode. All substrates were exposed under ozone plasma to improve surface hydrophobicity. Graphene oxide solution with a concentration of 5 wt% which prepared by Hummer's method [23] was bought from Graphene market.

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Pristine GO thin films of about 15–30 nm in thickness was spin coated on the substrates. After that, samples were annealed on hot plate at 100 °C for 1 h to remove the solvent. Then, the prepared GO film was thermally reduced at 250 °C within 2 h at ambient pressure on a hot plate or in vacuum** (about 6×10^{-6} Torr). Finally, Al or Au of 100 nm thickness was thermal evaporated as the top electrode.

Atomic force microscopy (AFM; Dimension 3100, Veeco) was used to observe the surface morphology of the deposited graphene oxide and *r*GO thin films. The transmittance and sheet resistance of graphene oxide and *r*GO thin films were measured by UV–Vis-NIR spectrophotometry (Carry 5000, Varian) and 4-probe measurement, respectively. The *I–V* curve, retention time, and endurance characteristic of the top electrode (TE)/active (GO or *r*GO)/bottom electrode (BE) sandwiches were measured using SourceMeter (2336 SMU, Keithley). The LRS and HRS were characterized in a frequency from 10 Hz to 10^5 Hz with 10 mV modulation by impedance spectroscopy (IviumStat, Ivium Tech.). All measured impedance data were simulated using ZView2 software.

3. Results and discussion

Fig. 1(a) shows the optical transmittance of fresh graphene oxide films of ~15 nm thickness on glass substrate, thermally reduced at 250 °C for 2 h in ambient pressure and in vacuum (6×10^{-6} Torr). Fig. 1(b)–(d) shows AFM images of pristine graphene oxide and *r*GO films reduced in different pressure, respectably. The pristine graphene oxide film is a dielectric layer with very high sheet resistance and high transmission (T = 79% @500 nm). *r*GO film reduced in vacuum exhibits slightly differed transmission. In contrast, an *r*GO film reduced in ambient pressure showed drastic changes in transmission. This variation may be due to the oxygen in the air that could react with graphene oxide and initiate the evolution of CO or CO_2 gases during thermal reduction process. Thus, the *r*GO film strongly reduced at ambient pressure led to low transmission (T = 50% at 500 nm) and low sheet resistance (R_s = 466 kΩ/sq.) when compared to *r*GO film reduced in high vacuum (T = 75% at 500 nm, Rs = 10 MΩ/sq.). In addition, the surface roughness value of *r*GO film reduced in air pressure is higher than that reduced in vacuum. The rapid increase of temperature on a hot plate causes oxygen-containing functional groups attached to the carbon plane to suddenly decompose into gases. So, *r*GO film reduced at ambient pressure might produce more wrinkled graphene sheets and surface roughness up to 4.93 nm, as showed in Fig. 1(c). In other substrates, such as ITO and Al, the roughness had the same trend showing dependence on the pressure during reduction process. But, in the case of Au, the *r*GO film has a large roughness with a wide deviation across the substrate surface (data not shown).

The schematic of structure and the current–voltage (*I–V*) curve in a semi-logarithmic plot of Al/rGO reduced in vacuum/Al device were shown in Fig. 2(a). The active layer of this device was fabricated with 15 nm of thickness. To characterize the electric performance of memory cells, a bias voltage was applied with constant rate from 0 to −4 V, then up by +4 V, and finally backs the initial state (0 V). The curve was swept by applying a bias to the top electrode and grounding the bottom electrode. To investigate the endurance of device performance, cyclic switching operations was conducted. Fig. 2(b) showed the evolution of resistance values read at −1 V in each DC sweep cycle. The retention performance did not show degradation up to 10^6 s, as shown in Fig. 2(c). In our experiment, the ON/OFF ratio for Al/*r*GO/Al was around 10.

We also investigated other combinations of top and bottom electrode (TE, BE) materials, active layer (initial GO, *r*GO reduced at the air, and *r*GO reduced in high vacuum) and the results are

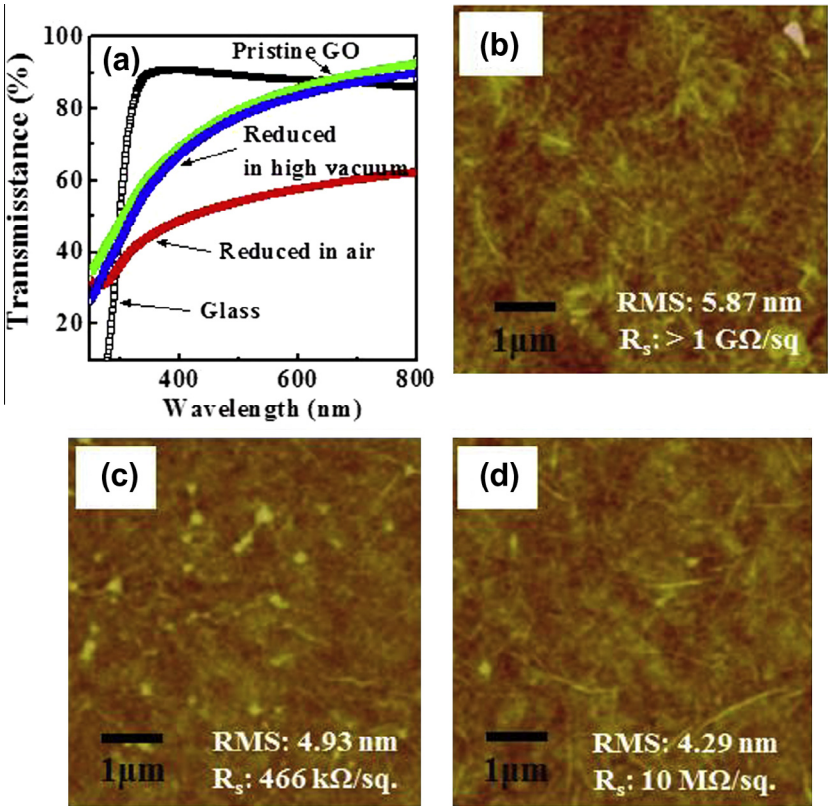

Fig. 1. (a) Optical transmittance spectra of flash GO film (15 nm) and *r*GO film reduced at different pressures. AFM images of surface roughness of (b) initial GO film, (c) *r*GO film reduced at ambient pressure, and (d) *r*GO film reduced in vacuum pressure.