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Reduced graphene oxide preparation and its applications in solution-processed write-once-read-many-times graphene-based memory device

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ABSTRACT

We fabricated graphene-based non-volatile memory device by solution-processed route in this work. Thermally reduced graphene oxide (rGO) on quartz substrate prepared in the ambient of acetylene/hydrogen plasma treatment was used as bottom conductive electrode to replace the commonly-used bottom conductive indium-tin-oxide layer. The morphology of the rGO film was characterized and used for device fabrication. The device was fabricated in the simple structure of silver nanowires/nanocomposite/rGO/quartz and the nanocomposite was prepared by mixing the graphene quantum dots and graphene oxide in ethanol. Current-voltage (I–V) measurement of the fabricated device shows current bistablity with the similar behavior as write-once-read-many-times (WORM) memory device. The ON/OFF ratio of the current bistability for the devices was as large as 1×10^3 with retention stability up to 1×10^4 s. The direct tunnelling, trapped-charge limited-current, and Ohmic conduction were proposed as dominant conduction mechanisms through the fabricated NVM devices based on the obtained I–V characteristics.

1. Introduction

The two-dimensional carbon nanomaterials, such as graphene have been widely explored recently to demonstrate its potential applications in biomedical study and by fabricating graphene-based nano-scaled electronic, optoelectronic, photovoltaic, and sensing devices [1–4]. Graphene has received significant research attention due to its unique properties of planar structure, high electrical conductivity, high transparency and flexibility, large surface area, and high mechanical stability [5–7]. Moreover, its advantages of high density of states, high mobility, high work function, and low dimensionality compared with the conventional charge trap materials [5,8] suggest that graphene can be used as the potential material in non-volatile memory (NVM) devices as the charge trap medium [4,5,9,10].

For enhancing memory data retention in real applications, the nanometer-sized graphene pieces such as graphene quantum dots (GQDs) would be preferable to be integrated for device fabrication owing to the discrete charge trap materials offers the advantage of constricting lateral charge movement as a result of the nanocrystals are separated from each other [5,11]. Consequently, GQDs will be used as a discrete charge trap medium in this work. Even though some investigations of the NVM devices fabricated with GQDs by using a solution process route have been conducted [8,10], studies on the device performances by incorporating GQDs in the graphene oxide (GO) matrix with reduced graphene oxide (rGO) prepared by acetylene/hydrogen (C_2H_2/H_2) plasma treatment as a bottom conductive layer to realize fully graphene-based materials NVM devices have not yet been performed.

GO the non-conducting material will be used to replace the solution polymer matrix as it does not require high temperature

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treatment after the deposition process and the nanocomposite mixture offering the potential of cost-effective, large-scale production, environmental friendliness and simple method to develop graphene-based electronic devices [12–14]. Meanwhile, the commonly used bottom conductive indium-tin-oxide (ITO) layer will be replaced by conductive rGO thin film owing to the costly ITO attributed to the limited rare element of indium. It is also mechanically brittle, chemically unstable and poor adhesion to organic materials [15–17]. Alternatively, rGO also provides an excellent conductivity and transparency but more importantly better chemical stability and flexibility than ITO [18]. However, the quality of typical rGO lattice is much lower compared to that of a CVD grown graphene due to high structural defects, such as vacancies and topological defects after reduction [19]. Thus far, only little progress has been made to improve the graphitic structure by healing of the lattice defects to produce high-quality rGO with excellent electrical performance [20,21].

Therefore, in this study, the rarely reported thermal reduction method with C_2H_2/H_2 plasma treatment will be used to produce high-quality and conductive rGO thin films from the synthesized GO solution on the quartz substrate. The advantage of C_2H_2/H_2 plasma treatment is to heal the lattice defects of rGO by the addition of carbon atoms in clustering of the sp^2 domains. Then, the two-terminal, fully graphene-based NVM device, in the simple metal-insulator-metal (MIM) structure of silver nanowires/nanocomposite/rGO/quartz will be fabricated using fully solution-processing route. Solution-processing deposition techniques are particularly attractive because of interest in realizing transparent and flexible electronic devices without the need of complicated fabrication processes that require expensive vacuum equipment, high-temperature fabrication steps and high manufacturing cost [10,22,23]. The rGO and nanocomposite mixture will be deposited using the spin-coating method while the top metal electrode contact could be formed by the spray-coating method to avoid the expensive and time-consuming metal vacuum evaporation process [22].

2. Experimental

In this study, the bottom conductive rGO thin film was derived from the synthesized GO flakes. GO was synthesized from graphite powder using a typical modified Hummer's method [24]. The GO flakes suspended in ethanol with a concentration of 1.0 mg/mL were ultrasonicated for 30 min to obtain a homogeneous GO solution. The GO flakes were then deposited on the 1 cm × 1 cm quartz substrate by the spin-coating method at a rate of 3000 rpm for 40 s. At this rate, the solvent was rapidly evaporated, thus leaving the 5 nm thick GO flakes on the substrate in the form of thin film due to the strong van der Waals forces interaction. The reduction of GO film was begun by thermal annealing at 700 °C under vacuum atmosphere for 6 h to effectively diminish a substantial amount of oxygen functional groups in the carbon network. By maintaining the temperature of 700 °C, the rGO film was carefully plasma-treated using a mixture of C_2H_2/H_2 gas at a flow rate of 40 sccm/10 sccm and a plasma power of 20 W for 2 min. This process is inferred to improve the carbon crystalline structure from the substitution of carbon atoms in the aromatic hexagonal lattice of graphene. The morphologies of the rGO film on the substrate were characterized prior to device fabrication.

The nanocomposite mixture was prepared by mixing the GQDs in ethanol (1 mg/ml) purchased from ACS Material and the synthesized GO solution with the volume ratio of 2:1 and agitated for 15 min to ensure the homogenous distribution of the GQDs in the GO solution matrix [Refer to Fig. S1 in Supplementary Material for the nanocomposite characterization]. Then, a 7 nm thick nanocomposite layer was then spin-coated at 2500 rpm for 40 s on top of the rGO film and a reference device without GQDs also fabricated with the same spin-coating condition. Finally, the top silver nanowires (Ag NWs) electrodes were spray-coated with the aid of 0.5 mm diameter circular shadow mask at 0.1 MPa on a 100 °C hot plate to complete the graphene-based devices structure of (a) AgNW/GO/rGO/quartz and (b) AgNW/nanocomposite/rGO/quartz, denoted as reference device and NVM device. Ag was used as the top metal contact in this work due to it is a renowned low-cost metal yet from the same noble metal category as compared with Au [25]. Additionally, Al was not used as it yielded a higher turn-on voltage in our earlier reported work [26]. Fig. 1 shows the schematic diagram of the fabricated devices whereas the inset in Fig. 1(b) shows the transmission electron microscopy (TEM) cross-sectional image for the fabricated NVM device.

The morphologies of rGO film on the substrate were characterized by a field emission scanning electron microscopy (FESEM) system (JEOL, JSM 7500 F) operated at an accelerating voltage of 2.0 kV, a high-resolution transmission electron microscopy (HRTEM) system (JEOL, JEM-2010) operated at an accelerating voltage of 200 kV, and an atomic force microscopy (AFM) system in a semi-contact mode (NTEGRA Spectra, MT-MDT). For the HRTEM studies of rGO film, the sample was prepared by dipping a carbon-coated TEM grid into the GO solution and allowing it to dry at room temperature. The reduction of the sample was then carried out by the same reduction method to the as-prepared rGO/quartz substrate. Meanwhile, the FEI Tecnai TF20, a 200 kV FEG HRTEM was used to obtain the cross-sectional structure of the fabricated device. The samples of GO, before and after reduction with C_2H_2/H_2 plasma treatment have been characterized by X-ray photoemission spectroscopy (XPS) system (Scanning XPS Microprobe, PHI Quantera II), ultraviolet–visible (UV–vis) spectroscopy system (Agilent Cary 7000), and Raman spectroscopy system (NTEGRA Spectra, MT-MDT). For the electrical measurements, the rGO/quartz sample was cut into a square shape with size of 1 × 1 cm^2. The electrical properties of rGO films were measured with a Hall-effect measurement system (Ecopia, HMS-5300) based on the van der Pauw method. Four contacts were made by soldering indium dots of about 0.5 mm on each of the edge of sample to create ohmic contact with rGO films. The current-voltage (I–V) measurements of the fabricated NVM devices were performed at room temperature by using Keithley 4200-SCS semiconductor characterization system. Bias voltages were applied to the bottom rGO electrode with respect to the top metal electrode for all measurements.

3. Results and discussion

Fig. 2(a) shows the FESEM image of rGO films prepared on quartz substrate with flake size up to 50 μm. It was observed that the rGO flakes are of unsymmetrical shape in random multi-stacked order due to the van der Waals interactions. The visibility color contrast of rGO films indicates that it consists of few layers. The TEM image in Fig. 2(b) clearly shows the presence of mostly few-layered and folding-structured rGO films, which is almost electron transparent from its low magnification image. Interestingly, the HRTEM images in Fig. 2(c–d) reveal the periodic bright spots in the rGO films, suggesting the significant restoration of sp^2 carbon domains in the carbon crystalline lattice after plasma treatment in the C_2H_2/H_2 ambient [27]. It should be noted that few portion of the rGO films (indicated by blue box) show clear Moiré patterns in the HRTEM image arising from rotational stacking faults (see Fig. 2(c)), indicating the van der Waals nature of such rGO films [28]. However, the characteristic of hexagonal atomic lattices with an estimated carbon–carbon bond length (a_{cc}) of ~1.4 Å and a lattice spacing (a) of ~2.4 Å are clearly observable in the HRTEM image