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Studies on resistive switching characteristics of aluminum/graphene oxide/semiconductor nonvolatile memory cells

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ABSTRACT

We report semiconductor-based resistive switching nonvolatile memory devices with graphene oxide (GO) as an active layer which is sandwiched between aluminum (Al) metal and semiconductors such as Si and Ge. Semiconductors (p-Si or p-Ge) are used as bottom electrodes on which a layer of GO is deposited and Al electrodes are then formed on the top of it by thermal evaporation. From current–voltage characteristics, it is found that the devices show diode like rectifying switching behavior, which can suppress the cross talk between adjacent cells. In these structures, during initial voltage biasing, the current conduction is found to be due to thermionic emission and in later stages, it is driven by space charge. The maximum on/off ratio in Al/GO/p-Si and Al/GO/p-Ge structures is 110 (at −1.2 V) and 76 (at −1.7 V), respectively. However, breakdown occurs in the memory cells fabricated on p-Ge after switching to low resistance state due to lack of stable oxide at the interface between Ge and GO unlike in the cells on Si where stable native SiO_2 prevents such breakdown. The mechanism of resistive switching in semiconductor based memory cells has been explained using X-ray photoelectron spectroscopy and capacitance–voltage characteristics.

1. Introduction

Currently, nonvolatile memory devices are dominated by silicon based Dynamic Random Access Memory (DRAM). However in near future it would be difficult to further increase the density of memory cells in DRAM due to its technological and fundamental limitations [1]. Resistive switching Random Access Memory (ReRAM) devices with simple three layered metal/insulator/metal (MIM) cross-bar array structures got the attention of researchers as future of nonvolatile memory (NVM) devices due to their high density, low power consumption, fast non-destructive switching and simple fabrication process. Further these ReRAM devices are capable of functioning without any transistors in every memory cell [2]. In MIM structures, an insulator 'I' would be sandwiched between two electronic conductors where 'M' stands for metal or any non-metal with reasonably good electronic conductivity. The top and bottom electrodes have great impact on the electrical performance of MIM structures [3]. To accomplish reliable resistive switching (RS) the common practice is to use two different metals as top and bottom electrodes. Depending upon the nature of the materials and metal electrodes, the conducting filament could be formed/eliminated with the applied voltage bias. Resistive switching has been observed in various materials such as binary transition metal oxides (ZnO [4], NiO [5], ZrO_2 [6] and TiO_2 [7]), chalcogenides [8], organic materials (PVK, PI: PCBM [9] etc.), amorphous Si (a-Si) [10] and graphene oxide (GO) [11]. Recently Si based

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ReRAM is widely reported due to their technological advantages [12–14]. Hyun et al. reported metal/a-Si/p-Si based memory devices, compatible with the CMOS technology, in which formation/elimination of filament was observed inside an a-Si matrix [15]. As researchers are trying to fabricate carbon based integrated circuits (ICs) with graphene based transistors [16–19] for future device technology, graphene oxide, being an important derivative of graphene, is a suitable material for memory devices in carbon based ICs. Graphene oxide, a single layer of graphene attached by epoxides, alcohols, ketone, carbonyl and carboxylic functional groups [20] shows interesting electronic properties particularly for nonvolatile memory applications and posses a bandgap depending upon the ratio of oxygen functional groups to carbon atoms [21]. Due to attachment of oxygen functional groups, GO is hydrophilic in nature and easily dispersed in deionized (DI) water. Uniform, large area deposition of GO could be easily achieved by spin casting, Langmuir–Blodgett technique, drop casting, dip coating and vacuum filtration methods. The thickness of the thin film could be controlled by changing the concentration of GO in DI water [22]. Thus due to its unique structure and large area processing, GO is emerging as a potential material for NVM applications [23].

The first GO based NVM device was reported by He et al. [24] with Cu as top electrode and the authors predicted that the resistance switching is due to the desorption/adsorption of oxygen functional groups responsible for the formation/elimination of conducting filaments in GO matrix. Jeong et al. [25] carried out a systematic study on the origin of switching mechanism in GO matrix and the authors experimentally showed that the resistive switching behavior is attributed to the formation and elimination of conducting filaments by Al top electrode at Al/GO interface. Yi et al. [26] reported GO based write-once-read-many times memory element with LiF as interfacial layer between GO and top Al electrode. Kim et al. [27] reported GO based resistive switching with $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO), a conducting oxide as a bottom electrode in which the resistive switching was explained by the movement of oxygen functional groups at GO/PCMO interface. All the above mentioned devices are based on MIM structures in which cross talk between different memory cells is quite possible because of high reverse current in the device; and same amount of negative voltage has to be applied to switch the device from ON state to OFF state which is used for switching it to ON state. To avoid cross-talk, an additional rectifying device is introduced in each memory cell which further increases the complexity of the ReRAM [28].

In the literature GO based NVM devices with different metals as top and bottom electrodes has been studied [29], however, elemental semiconductors such as Si and Ge as bottom electrodes has not been reported. The purpose of semiconductor as bottom electrode in our work is to introduce the rectifying current–voltage (*I–V*) characteristics in the NVM cell. The two dimensionality of GO also permits scaling beyond semiconductor technology which would be helpful for high density fabrication. In our present work, we have chosen two elemental semiconductors, viz. Si and Ge (both p-type) as bottom electrodes and aluminum (Al) as the top electrode. Moreover, these two semiconductors have abundance in nature and they do not show any hysteresis of their own.

We have used GO as a resistive switching layer between the metal and the semiconductor. In our present investigation we report fabrication of Al/GO/Semiconductor (AlGOS) structures for possible memory applications. In our devices, Al/GO/Si and Al/GO/Ge, the formation and elimination of conducting filament occur in the amorphous GO matrix. The major difference between the earlier works reported in the literature and the present one is the use of metal-GO-semiconductor structures instead of metal-GO-metal structures. Another advantage of AlGOS structures is that they show diode like rectifying and resistor like switching behavior by virtue of which cross talk between adjacent memory-cells can be suppressed due to their intrinsic rectification characteristics compared to conventional MIM structures. Therefore no additional rectifying device is required in each memory cell to suppress the cross-talk between memory cells.

2. Experimental

2.1. Synthesis of graphene oxide

Graphene oxide was synthesized by Hummers′ method [30]. In this method, 2.0 g of graphite flakes (Alfa Aesar 99.95%) and 1.0 g of $NaNO_3$ (Merck 98.5%) were added to 46 ml of concentrated H_2SO_4 (Merck 98%) and stirred for 15 min. The mixture was placed in an ice bath and cooled to 0 °C and 6.0 *g* of $KMnO_4$ (Merck 98.5%) was added slowly without exceeding the reaction temperature to 20 °C with continuous stirring. Then it was stirred for 2 h at 35 °C. At this step the mixture was turned into black gel type slurry and 100 ml of DI water (18.2 MΩ-cm) was slowly added and this lead to huge exothermicreaction raising the temperature to 98 °C. However, external heat was provided to maintain the reaction temperature at 98 °C for 15 min. The mixture was cooled to room temperature and 12 ml of H_2O_2 (Merck 30% purified) was added until the color of the mixture changed to golden yellow and an additional 400 ml of DI water was added.

The mixture was filtered through Whatman (42, Ashless) filter paper, centrifuged at 4000 rpm for 2 h and supernatants were decanted away. The remaining material was washed with DI water and 10% HCl mixture to remove the metal ions and successively with DI water till it attains a pH value between 4 and 5. The solid, thus obtained, was dried in vacuum for 4 h at 55 °C and finally a dark brown colored GO powder is produced.

2.2. Fabrication of aluminum–graphene oxide-semiconductor structures

The synthesized GO was dispersed in 20 ml DI water with a concentration of 1 mg/ml. Four devices were fabricated with structures Al/Si/Al, Al/GO/Si/Al, Al/Ge/Al and Al/GO/Ge/Al. The Si or Ge substrates were first heated in trichloroethylene for 5 min to degrease the surface, followed by heating in acetone for 3 min to remove chlorine residue. Then the substrates were washed in methanol and finally thoroughly rinsed with DI water. We have not used any cleaning process to remove native oxide from the Si or Ge surfaces. Before the fabrication of memory cells, the carrier concentrations in Si (1.14×10^{16} cm^{-3}) and Ge (4.52×10^{16} cm^{-3}) substrates were