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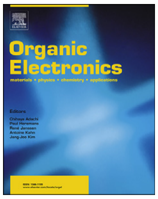

Nitrogen doped multilayer photo catalytically reduced graphene oxide floating gate: Al/PMMA/NrGO/SiO_2/p–Si/Au based hybrid gate stack for non volatile memory applications

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ABSTRACT

Photo catalytically assisted, multi–layer nitrogen doped reduced graphene oxide (ML–NrGO) is investigated as a promising charge storage layer in Al/PMMA/NrGO/SiO_2/p–Si/Au structure. A considerable memory window (ΔW) of ~3.3 V at ± 7 V sweep voltage and long data retention upto ~ 10^5 s is demonstrated as an encouraging candidature for emerging memory hierarchies. The clockwise hysteresis supports the hole charge trapping mechanism in the NrGO based structure. The ML–NrGO memory devices provide the rapid programming, saturation of the program transients, store more data at less cost and reduced ballistic transport in the plane perpendicular to NrGO. The facile, solution processable, cost effective device processing and stable retention of the fabricated ML–NrGO based Al/PMMA/NrGO/SiO_2/p–Si/Au flash memory structures proves to be a potential alternative for existing EEPROM based embedded applications and also for commercial scale production of flash memory based on flexible organic electronics.

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1. Introduction

With the advancement of semiconductor technology and scaling of device features size, excessive efforts have been devoted to develop an electrically re–programmable, high performance, low–cost floating gate based non–volatile flash–memory (FG–NVFM) devices, for popular consumer electronics [1]. The operation of FG–NVFM is particularly interesting and mainly relies on capacitance modulation at the trapping sites available in the FG [2]. With the continuous downscaling of FG for high–density data storage at low operating voltages, the FG–NVFM structures have encountered several challenges like enhanced capacitive/parasitic coupling within neighboring FG, variation in threshold voltages finally leading to critical concerns of device performance and reliability [1,3]. The scaling of FG–NVFM has already reached its threshold; hence, new materials/approaches are required to meet the current and futuristic demand of reliability and performance of FG–NVFM for electronics devices. Driven by this demand, thin metal layer (~1 nm) and nanoparticles were considered as an alternative in the past, owing to their quantum confined characteristics [2,4]. But, due to inherent band gap restriction, reliability and variability like agglomeration/diffusion of metal into dielectrics; the metal layer and nanoparticle based FG–NVFM shows relatively narrow memory window (ΔW) and short retention characteristics [2–4].

Recently, graphene (monolayer thickness of ~0.3 nm) with excellent electronic properties has emerged as a potential FG material to exceed the performance of FG–NVFM [5]. The considerations for use of graphene are (i) high density of states (DOS) (8×10^{12} cm^{-2} eV^{-1} for monolayer and 4.4×10^{13} cm^{-2} eV^{-1} for multi–layer, (ML)); (ii) high work function (~4.2 eV for monolayer and 4.6 eV for ML (3–4)), and (iii) low dimensionality [3,5]. The high DOS, work function and a reduced ballistic component of conductivity along the perpendicular plane, supports the large ΔW in ML graphene based FM [3,5]. To date, CVD graphene based FM has been demonstrated [1,5], however, besides expensive, the CVD graphene based FM may lead to failure of the device due to pin–-holes [1]. Therefore, the solution processed, low–cost, derivatives of graphene, graphene oxide (GO), reduced graphene oxide (rGO) with monolayer thickness $\leq$ 1 nm, has attracted substantial interest from the scientific community and used as an effective FG material, channel in FETs, super capacitor electrode and sensors [6–18].

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Structurally, GO consists of a hexagonal carbon ring network with sp^2 hybridized carbon atoms and sp^3 hybridized carbon and hydrophilic functional groups [9,13]. GO with functional groups shows insulating characteristics, while on reduction, results into rGO which is conducting in nature. Several strategies for the GO reduction and formation of rGO is discussed in past [11]. The presence of functional groups, defects, high DOS and work function in GO and rGO provides quantized levels and contributes to the charge storage applications, as reported in Refs. [3,4,7]. Additionally, other advantages of using GO–rGO sheets as FG includes, (i) the band gap modulation based on the degree of oxidation and reduction, hence tuning the physiochemical and electronic properties, (ii) solubility of GO in a wide range of solvents, allowing controlled deposition, followed by reduction to rGO. Even though, GO sheet decorated with functional groups is thermally unstable at temperatures (>300 °C) owing to loss of attached functional groups between adjoining GO sheets [7,19]. Hence, GO based devices pose a serious concern for Si technology, therefore, rGO is being thought as a probable alternative.

Beside this, efforts have been made in order to enhance the electrical conductivity of rGO. Hence, doping seems to be an alternative way for tailoring the electronic, physiochemical properties [20–22]. Thus, nitrogen (N) doping in rGO is considered to be an excellent choice owing to the comparable atomic size, transfer of charge carriers forms strong bonds with carbon atoms [21,23–25]. The detailed mechanism for the doping of nitrogen in GO, rGO is reported in past [26–29]. Generally, the doping introduces chemically active sites, owing to the interaction between the positive charge in the nitrogen and negative charge in functional groups present in GO, which leads to polarization under electric filed, hence, the active sites and ease of polarizability in NrGO can be advantageous for memory storage applications [29–31]. However, existing N doping techniques, generally involve toxic reagents, ambient conditions, dedicated setup, are expensive and require high temperatures processing [21,22,24,32]. Therefore, the need of the hour is to explore a rapid, inexpensive, environment–friendly and scalable approach for the production of N doped GO/rGO for its use as FG in NVFM.

To address these challenges, the present work demonstrates a facile, cost effective, solution processable, photo–catalytic approach for the synthesis of engineered, multilayer nitrogen doped reduced graphene oxide (ML–NrGO) formulation, useful as FG material in Al/PMMA/NrGO/SiO_2/p–Si/Au, NVFM. In this work, we systematically investigated the charge storage capability and retention for the NrGO based Al/PMMA/NrGO/SiO_2/p–Si/Au FG–NVFM structures. The multilevel memory characteristics are measured using capacitance–voltage (C–V) characteristics with low sweep voltages of ±7 V. Subsequently, the leakage characteristics are evaluated by the current density–voltage (J–V) characteristics, while, the retention characteristics of the fabricated FG–NVFM structure is estimated based on the capacitance–time (C–T) measurements at room temperature.

2. Material and methods

2.1. Materials

All chemicals were of analytical grade and used without any further purification. Graphite powder (99.999% pure, size < 100 μm), Ethanol, Hydrogen Peroxide (H_2O_2), Sodium Nitrate ($NaNO_3$), Ammonia solution (NH_3 ~ 25%), Potassium permanganate ($KMnO_4$), Hydrochloric acid (HCl) were purchased from Merck. Sulphuric acid (H_2SO_4) and NMP from Fisher Scientific and Alfa Aesar. De–ionized (DI) water (Elga make, UK) resistivity of 18.2 MΩ cm was used in the present study for cleaning, solution preparation and dilution. UV lamp source (130 w, 253 nm, G64HO75, Arklite make) with an intensity of ~10 mW/cm^2 at distance of ~6 cm (measured by UVC Light Meter 850010, SPER Scientific make), was used as a source for the NGO reduction. During the exposure, the temperature of the UV chamber was maintained below 40 °C to avoid thermal reduction of GO.

2.2. Synthesis of GO and NGO

The synthesis of GO was carried out based on modified Hummers method, as reported in past [13,33]. To a brief note, the graphite powder is subjected to oxidation under constant stirring and the reaction is carried out in an ice bath (<5 °C) to result into graphite oxide. To obtain GO powder, the graphite oxide solution was consecutively centrifuged, washed with DI water until pH ~7 and finally dried in a vacuum oven. The aqueous GO solution (~1 mg/ml) in DI water was prepared using mild sonication for 120 min. For N doping in GO, NH_3 solution (~150 ml) was added to the GO solution, kept on a hot plate at 50 °C under constant stirring for 72 h, finally drying the solution in vacuum oven result in brownish NGO powder. During doping of nitrogen, the NH_3 molecules are expected to react more with the hydroxyl (–OH) and epoxy functional groups in GO rather than on the carbon surface, owing to the requirement of low formation energies for reaction between functional groups (~2.51 eV) and nitrogen rather than with carbon (~5.61 eV) [27], hence leading to the formation of pyridine–N as compared with pyrrolic and graphitic N [26,27]. The reaction of N with the functional groups results into water molecule and NH_2, further adsorbed on the carbon surface [26,29]. Additionally, it is reported that the interaction between pyridine N and charged carboxylic functional group in NrGO induce polarizations under an electric field, hence results into ON and OFF state for memory devices [29].

2.3. Fabrication of Al/PMMA/N–rGO/SiO_2/p–Si/Au FG–NVFM

A 2 inch, p–type Si wafer (1–10 Ωcm) with ⟨100⟩ orientation was cleaned using standard RCA cleaning. For high quality, tunnel oxide growth, the cleaned Si wafers were subjected to Rapid Thermal Oxidation (RTO) using AS – One RTP System (ANNEALSYS, France Make) from room temperature to 900 °C under N_2 followed by O_2 at 800 sccm, for 90 s (as shown in Fig. 1). The ramp up and down conditions was maintained around 25 and 3 °C/sec, respectively. The thickness of the RTO grown SiO_2 was measured by J. A. Woolman Imaging Ellipsometer and found 5 ± 0.2 nm. Thereafter, Au (~100 nm) bottom contact was made using e–beam evaporator after etching the back side buffer oxide to result into SiO_2/p–Si/Au. The as synthesized NGO powder was dispersed in DI: Ethanol in a ratio (1:2) and spin–coated onto SiO_2/p–Si/Au wafer at 2000 rpm for 45 s at an acceleration of 100 rpm/sec and dried at 50 °C for 3 min. The NGO is dispersed in a mixture of DI: Ethanol, as GO forms stable, uniform dispersion with DI water and ethanol [34], which finally results in deposition of uniform NGO film over SiO_2/p–Si/Au substrates. After drying, NMP (~10 μl) was drop casted on NGO/SiO_2/p–Si/Au and heated at 70 °C for 4 min. For the photo catalytic reduction, the NGO/SiO_2/p–Si/Au samples were then subjected to UV irradiation for 45 min and sample to UV tube distance was ~6 cm and later on, PMMA (950 A1) was spun coated, at 1000 rpm for 60 s at an acceleration of 100 rpm/sec, and dried at 80 °C for 5 min. The thickness estimate for PMMA was performed using NanoMap–LS (AEP Technologies, USA) and was found to ~ 50 nm.

Finally, the PMMA/NrGO/SiO_2/p–Si/Au samples were subjected to top metal, Al deposition (thickness ~150 nm) under high vacuum at ~ 1.5×10^{-6} mbar and the Al is patterned with standard lithography. Fig. 1 (a) shows the schematic process flow for the

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