Supporting Information

High-k Polymer/Graphene Oxide Dielectrics for Low-Voltage Flexible Nonvolatile Transistor Memories

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1. Experimental methods

1.1 Material.

Poly(methacrylic acid) (PMAA) was purchased from Scientific Polymer Products, Inc. (cat# 709). The molecular weight ($M_n$) of PMAA measured via gel permeation chromatography (GPC) eluted with DMF solution was 180000 g/mol with polydispersity index (PDI) of 1.8. Graphene oxide (GO) dispersion in water at a concentration of 500 mg L$^{-1}$ was purchased from Polymer Source Inc.

1.2 Preparation of Graphene Oxide and PMAA nanocomposite.

To make the well-dispersed mixture and facilitate the hydrogen bonding, PMAA and GO mixed in water solution was stirred overnight and then spin-coated onto a pre-cleaned ITO-PEN (polyethylene naphthalate(PEN)) substrate at 1000 rpm for 60 s. The thickness of the composite thin film was determined to be 50–60 nm.

1.3 Fabrication of the blocking gate dielectrics thin film.

Poly-4-vinylphenol (PVP) was prepared with a cross-linking agent 4,4’-(hexafluoroisopropylidene)diphtallic anhydride (HDA) by weight in propylene glycol monomethyl ether acetate (PGMEA). The concentrations of PVP and the HDA are 20 and 2 mg mL$^{-1}$. A catalytic amount of triethylamine (TEA) 2% was added to the
solutions of PVP with anhydride cross-linkers to promote the esterification reaction.

The solutions were filtered through a 0.2 mm syringe filter and spin-coated onto ITO-PEN substrates at rates of 4000 rpm for 1 min. The thickness of the cPVP film measured by surface profiler 100–120 nm.

1.4 Fabrication of the TIPS-pentacene OFET Memory Devices.

The transistor-type memory devices based on a TIPS-pentacene thin film were fabricated on ITO-PEN as a gate electrode. The solution of PMAA-GO nanocomposites was spin-coated at 1000 rpm for 60 s on cross-linking PVP surface. Thereafter, the polymer thin films were dried under vacuum (10^{-6} torr) at 100 °C for 1 h to remove residue solvents. The thickness of the prepared thin film was estimated to be 65–70 nm. The thin film of TIPS-pentacene was dissolved in THF at a concentration of 10 mg mL^{-1} and then spin-coated onto PMAA-GO nanocomposites at 1000 rpm for 60 s and baked at 80 °C for 1 h under vacuum to form a 50-nm-thick film. The top-contact source and drain electrodes were defined by 80 nm-thick gold through a regular shadow mask, and the channel length (L) and width (W) were 50 and 1000 μm, respectively. The current-voltage (I–V) characteristics of the devices were measured by using a Keithley 4200-SCS semiconductor parameter analyzer in a N₂-filled glove box.
1.5 Characterization

Atomic force microscopy (AFM) measurements were obtained with a NanoScope IIIa AFM at room temperature. Commercial silicon cantilevers with typical spring constants of 21-78 Nm$^{-1}$ was used to operate the AFM in tapping mode. The morphology of the prepared PMAA-GO was characterized by the transmission electron microscope (TEM, JEOL 1230). The thickness of polymer film was measured with a Microfigure Measuring Instrument (Surfcorder ET3000, Kosaka Laboratory Ltd.). X-ray diffraction (XRD) was performed by X’Pert PRO X-ray diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å) with a scan range typically of 5 - 30 degrees, 0.2 degrees per step. The electrical characterization of the memory device was performed by a Keithley 4200-SCS semiconductor parameter analyzer in a glove box. For the capacitance measurement, metal-insulator-semiconductor (MIS) structure was fabricated by depositing gold electrodes on the ITO-PEN substrate. The capacitance of the bilayer dielectrics was measured on the MIS structure using Keithley 4200-SCS equipped with a digital capacitance meter (model 4210-CVU).
2.1 Mobility

The field-effect mobility is estimated from the plot of the square root of drain-to-source current \((I_{ds})^{1/2}\) versus the gate voltage \((V_g)\) by the following equation in the saturation regime:

\[
I_{ds} = \frac{WC_{poly}\mu}{2L} (V_g - V_{Th})
\]  

(1)

where \(\mu\) is the field-effect mobility, \(C_{poly}\) is the gate dielectric capacitance per unit area and \(V_{Th}\) denote the threshold voltages. The capacitances \(C_{poly}\) of the different gate dielectrics were measured at 10 kHz.

2.2 Capacitance

The relations between capacitance \((C_{Tot})\) of the device, blocking layer \((C_{cPVP})\), polymer electrets \((C_{poly})\) and polymer dielectric constant \((\varepsilon)\) are defined as the following:

\[
\frac{1}{C_{Tot}} = \frac{1}{C_{poly}} + \frac{1}{C_{cPVP}}
\]  

(2)

\[
C_{poly} = \frac{\varepsilon_o\varepsilon}{d}
\]  

(3)

where \(\varepsilon_o\) and \(d\) are the vacuum permittivity and the insulator thickness.

2.3 Estimate the amount of stored charges
The shifts in memory window ($\Delta V_{Th}$) can be used to estimate the amount of stored charges ($Q$) according to Equation (1):

$$\Delta V_{Th} = -\frac{d_i Q}{\varepsilon_i} = \frac{Q}{C_i}$$  (4)

where $C_i$ and $d_i$, $\varepsilon_i$ are the capacitance of total dielectrics, the thickness and dielectric constant of the polymer electret layer, respectively.
Fig. S1 Atomic force microscopy (AFM) topographies of (a) PMAA-GO1.5, (b) PMAA-GO3, (c) PMAA-GO6, and (d) PMAA-GO12 on ITO-PEN substrates on the 1 μm x 1 μm area.
Fig. S2 Leakage current of the device using cPVP and cPVP/PMAA-GO3 films.
Fig. S3 The capacitance of PMAA.

The capacitance of PMAA is shown as a function of voltage. The thickness of the sample is 40nm.
Fig. S4 Transfer characteristics of the memory devices with PMAA-GO3 as charges storage layer.
Fig. S5 Transfer characteristics of the memory devices with PMAA as charges storage layer.
Fig. S6 (a) The mobility and (b) the memory window of the flexible memories with PMAA-GO3 charges storage layer as a function of the number of bending cycles.