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Graphene quantum dots as shallow traps in a high-k polymer matrix for bipolar resistive switching

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Abstract
Graphene quantum dots (GQDs) have broad applications in electronic and photonic devices. As a typical zero-dimensional material, a GQD has a stronger quantum confinement effect than do two-dimensional graphene or one-dimensional graphene nanoribbons, and provide efficient charge trapping sites, which are useful in nonvolatile memory devices. Here, we report the fabrication of 30-nm-thick GQD-blended high-k polymer cyanoethylated pullulan (CEP) thin films sandwiched between an Al top electrode and an indium tin oxide (ITO) bottom electrode. Bipolar resistive switching behavior was observed with a low onset (−1.7 V) and offset (1.3 V) voltages. The resistive switching behavior originates from shallow traps that induce space-charge-limited current conduction. The morphology, crystallinity and photoluminescence of the GQDs were also studied by atomic force microscopy, transmission electron microscopy, and photoluminescence spectroscopy. The CEP/GQD blended films may have applications in nonvolatile resistive memory devices.

Introduction
Resistive random access memory (ReRAM) has potential applications in non-volatile memory (NVM) devices. It has exceptional scalability to nanometer feature size [1], high switching endurance [2, 3], low power consumption [4] and fast operation speed of nanoseconds [5, 6], and is therefore regarded as a substitute for flash memory. Inorganic materials with high dielectric constant k such as NiO [7], TiO2 [8], HfO2 [9], which have been used as gate dielectric materials to supersed conventional silicon dioxide to achieve continuous complementary metal–oxide–semiconductor (CMOS) scaling. However, organic storage media, which usually have low fabrication cost and high mechanical flexibility, have been assessed as promising materials for application in NVM devices. Hybrid designs combing superiorities of organic and inorganic materials have been used for ReRAM applications [10, 11].

A typical polymer-based memory device consists of a nanoparticle (NP)-incorporated polymer layer sandwiched between two metal electrodes. Various metallic NPs (e.g., Au, Ag) [12] and semiconductor quantum dots (QDs) (e.g., GeSe, core–shell ZnSe/ZnS, PbS and MoS2) [13–16] have been evaluated. Compared to conventional NPs, graphene quantum dots (GQDs) have unique properties such as abundant availability, non-toxicity, high solubility, size-dependent and excitation-dependent optical response, tunable bandgap due to chemical functionalization, electrochemical properties, and charge storage capabilities [17–19], which suggest that GQDs may have application in data storage devices. As the polymer thin film matrix, several low-k polymeric materials have been applied, such as poly(methylmethacrylate) (PMMA, k∼2.3) [20, 21], polyvinylcarbazole (PVK, k∼3) [22, 23], polystyrene (PS, k∼2.5) [24, 25], poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS, k∼3) [26, 27]. However, utilization of high-k polymers for this purpose has not yet been demonstrated, which induce much improved build-in electrical field when similar thickness and voltage bias are applied [28–32].
In this paper, we use a blended thin film of GQD and a high-k polymer cyanoethylated pullulan (CEP) in an Al/GQD-CEP/ITO sandwich structure (figure 1, left). The GQD serve as shallow traps in the thin film to induce SCLC conductance. Resistive switching (RS) behavior and its mechanism are studied. The morphological properties of GQDs and the thin films are also investigated.

Experimental

Solutions were prepared in N,N-dimethylformamide (DMF) with 1 wt.% CEP (Mw ~ 489,000, Shin Etsu Chemical Co.) and with or without GQDs (synthesis process according to literature[28]). The solutions were spin-coated onto pre-cleaned indium tin oxide (ITO)-coated glass pieces at 3000 rpm for 60 s, then baked in a vacuum oven for 1 h at 80 °C. Al top electrodes were deposited by evaporation through a shadow mask to make a circular dot area of 8.02 × 10⁻³ cm².

Dielectric film thickness was measured by cutting the device with a focused ion beam (FIB) and observing the cross-section of the structure using a scanning electron microscope (SEM). The thicknesses of CEP/GQD film and the Al top contact film was about 30 nm and 100 nm, respectively. Surface morphology was studied using an Atomic Force Microscope (AFM; Dimension™ 3100 microscope, Digital Instruments). High-resolution Scanning Transmission Electron Microscope (STEM) and Transmission Electron Microscope (TEM) images with were obtained using a TEM (JEOL JEM-2100FS) located at the National Institute for Nanomaterials and Technology in Pohang, South Korea. Raman spectroscopy was performed using a confocal Raman microscope (Alpha 300R, WITEC). The electrical transport properties were tested using a probe station in an N₂-filled glove box. The current-voltage (I–V) data were collected using a Keithley 4200 semiconductor parameter analyzer.

Results and discussion

GQDs (figure 1, top right) are single- or few-layer graphene fragments with nanometer size. We used GQDs that have abundant –COOH groups on their side edges; these groups promote GQD solubility in polar solvents and
provide trap sites for charge storage and release. CEP (figure 1, bottom right) is an insulating polymer with $k \approx 19$ at 1 kHz [33], which makes it a promising candidate gate dielectric for organic field-effect transistors [34, 35]. It is usually synthesized by substituting cyanoethyl ethyl for the proton in the hydroxyl functional groups of polysaccharide. The cyanoethyl group in the side chain of the polysaccharide in CEP shows a large polarity and thus leads to a high $k$.

AFM images of GQDs dispersed on cleaned 300-nm SiO$_2$ coated silicon wafer were captured to image the height and roughly the size of the GQDs (figure 2(a)). The cross-sections of two typical GQDs were profiled; their estimated heights were ~1.27 nm (figure 2(b)) and ~1.49 nm (figure 2(c)), respectively. This is slightly higher than that of single-layer graphene [36], and may be due to the rough edges that have dangling functional groups.

To further investigate microstructural morphology, 100-times diluted GQD solution was dispersed onto a polycarbon-coated copper grids and vacuum pumped for 10 h at 40 °C. The GQDs had uniform size, with diameters in the range of 2–6 nm (average ~4 nm) with lattice spacing of ~0.21 nm (figure 3(a), figure S2 available online at stacks.iop.org/MRX/8/056304/mmedia). At high magnification the GQDs are approximately circular (figure 3(a)), and show clear patterns at highest magnification (figure 3(b)), which indicate that individual GQDs are highly crystalline.

Raman spectroscopy (figure 4) was used to analyze the GQDs, with chemical-vapor-deposited (CVD) graphene as a reference [37]. The CVD-grown graphene had a negligible D peak, which indicates that the graphene sheet had few defects; this sample also clear 2D peak at ~2685 cm$^{-1}$ that is caused by second-order zone boundary photons, a G peak at ca. 1590 cm$^{-1}$ that is caused by in-plane optical vibration. In contrast, in the GQD samples had abrupt D peak because of abundant functional groups and defects on the edges; due to this
variation at the edges, the 2D peak of GQDs was drastically broadened. A slight upshift in the D band of the GQD in comparison with the CVD-grown graphene reference implies p-type doping, probably by COOH and other functional groups (figure S1).

To investigate the optical properties of the GQDs, PL spectra were recorded after activation with various incident-light wavelengths (figure 5). The PL intensity peaks shifted to longer wavelengths as the excitation wavelengths were increased from 400 nm to 500 nm in 50-nm steps; this trend indicates that the as-prepared GQD exhibits excitation-dependent photoluminescence behavior, which is an important feature of many fluorescent carbon-based nanomaterials. PL intensity increased with the excitation wavelength. PL intensity is highly sensitive to various factors; mixed graphene fragments of different sizes may exhibit different excitation and emission spectra, because the gap decreases as QD size increases. The thickness of graphene layers also influences the spectroscopic properties of GQDs [38].

To investigate the electrical behavior of Al/CEP-GQD/ITO sandwiched structure (figure 6(a)), I–V plots were recorded during voltage sweep cycles between 2 V and −2 V (figure 6(b)). During the negative bias on Al top electrode sweeps from 0 V to −2 V, a sudden increase in current was observed at a voltage of approximately −1.7 V. This change indicates transition from a high resistance state (HRS) to a low resistance state (LRS); this is known as a set process. When the bias was swept back from −2 V to 0 V, the device stayed in LRS. During a positive sweep from 0 V to 2 V, an abrupt decrease in current occurs at ∼1.3 V. This change indicates that the
device switched from LRS to HRS; this is known as a reset process. The LRS was maintained as the bias returned from 2 V to 0 V. Therefore, the device displays bipolar RS characteristics with a set voltage $\sim 1.3$ V and a reset voltage $\sim -1.7$ V. These $I$–$V$ plots of Al/GQD-CEP/ITO memory device demonstrate typical bipolar resistive switching behavior. The process could be repeatedly operated with negligible variation in the set and reset voltages. At a reading voltage of 0.3 V, on-off current ratio of 100 was obtained.

To investigate the resistive switching mechanism in Al/CEP-GQD/ITO sandwiched structure, the negative parts of the $I$–$V$ curve were re-plotted on a double-logarithmic scale (figure 6(c)). Several models have been presented to understand the carrier transport in electrode-insulator (or semiconductor)-electrode sandwich
structure, such as Ohmic conduction, Thermionic emission, Frenkel-Poole emission, and Space-Charge-Limited Current (SCLC) conduction [39]. Each model has distinctive I–V characteristic, which can be distinguished by the isothermal I–V correlation [40], for example, $I \propto V$ for Ohmic conduction, $\ln(J/V^2) \propto V^{1/2}$ for Thermionic emission, and $\ln(J/V) \propto V^{1/2}$ for Frenkel-Poole emission. For SCLC model, there exists different stages: for trap-free SCLC, the I–V characteristic can be described by Child’s Law: $J = \varepsilon \mu V^2 / 8d^3$, where $\varepsilon$ is the insulator dynamic permittivity, $\mu$ is the carrier mobility, and $d$ is the insulator thickness.

Based on the fitting results, the J–V characteristics in HRS follow linear Ohmic behavior at low bias, with the addition of a quadratic term at higher bias ($I \propto aV + bV^2$), which is typical of an d insulator with shallow traps and SCLC injection [41–43]. At low applied bias, Ohm’s law dominates the I–V characteristics because the concentration of carriers injected from the electrode is negligible compared with the concentration of thermally-generated free electrons. As the applied bias increases, the number of injected carriers becomes large and they are captured by shallow charge traps in the GQD, so the current enters the shallow-trapping field region. As the applied bias is increased further, the injected carrier density becomes large enough to fill all trapping sites in GQDs, so additional injected carriers at still higher bias contribute directly to conduction, thereby resulting in a significant increase in currents, so the J–V curve follows Child’s Law ($I \propto V^2$), as shown in the high voltage HRS region (the slope is ~2.04). For LRS at low voltage, current depends linearly on voltage with a slope of ~1.02; this slope indicates that the I–V curve obeys Ohmic conduction ($I \propto V$). In summary, the carrier transport mechanism experiences the process of (1) Ohmic conduction, (2) SCLC conduction with shallow traps, (3) SCLC conduction with filled traps (4) Ohmic conduction. Thus, the bipolar switching behavior can be explained by shallow trap-controlled SCLC model due to the charge trapping/de-trapping process in this GQD-based nanocomposite.

Conclusion

Resistive switching behavior was observed in a CEP polymer/GQD blended 30-nm-thick film. This is a first evaluation of high-κ polymer cyanoethylated as the polymer matrix for resistive switching devices. GQDs with uniform size distribution provided sufficient shallow traps for nonvolatile resistive switches. The mechanism of the as-fabricated memory device originates from charge trapping and de-trapping in GQD-based nanocomposite. The morphology, crystallinity, Raman spectroscopy and photolumenecence properties of the GQDs were characterized in detail. This work may extend the application of GQDs for memristive devices.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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