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Size Modulated Nitrogen-Doped Graphene Oxide Quantum Dots for Diffusive Memristor based Synaptic Device Applications

Andrey S. Sokolov, Yu-Rim Jeon, Hoonhee Han, Boncheol Ku, Gul Hassan, Haider Abbas, and Changhwan Choi*
Division of Materials Science and Engineering, Hanyang University, Seoul 04763, Republic of Korea
*Phone: +82-2-2220-0383 *E-mail: cchoi@hanyang.ac.kr

Abstract

We report an electronic synapse based on threshold switching (TS) phenomenon by silver ion migration diffusive dynamics in Ag/N-GOQDs/Pt device, where nitrogen-doped graphene oxide quantum dots (N-GOQDs) with different sizes ranging in 0.5 ~ 12 nm as thin film serve for a memory storage medium. Among all, TS device with 3~6 nm sized N-GOQDs possesses the best thin film self-assembly ability, leading to the reliable TS behavior. Further, important bio-synaptic functions are successfully emulated in the device, such as short-term memory (STP), long-term memory (LTP), and STP-to-LTP memory transition.

1. Introduction

Neuromorphic computing as a future computing paradigm can simultaneously combine information processing and memory storage to overcome the limitations of conventional von Neumann computing [1]. To realize neuromorphic systems, the bio-similar synapses should be well-emulated by artificial electronic synapses in terms of size, power and synaptic functioning. Accordingly, many devices based on resistive switching (RS) phenomenon have been investigated for the next-generation memory and artificial electronic synapses [2,3]. Among these devices, a two-terminal device with silver ion (Ag^+) diffusive dynamics in inorganic/organic ionic conductor matrix was shown to closely emulate physical behavior similar to bio-synaptic Ca^{2+} dynamics [4,5,6].

In this study, to date, we fabricated and investigated resistive threshold switching (TS) characteristics in Ag/N-GOQDs/Pt device by utilizing nitrogen-doped graphene oxide quantum dots (N-GOQDs) with categorized different sizes (0.5 nm ~ ~12 nm) of QDs and the best TS performance is obtained with QDs having 3 to 6 nm size for the synaptic memorization medium. It is found that N-GOQDs with size range of 0.5 ~ 6 nm exhibits TS behavior. The improved TS behavior is observed with thicker QD size (3 ~ 6 nm) in terms of reliability/stability of TS characteristics and lower threshold voltage (V_{th}~<0.18V) switching. Moreover, the core synaptic functions of biological synapse such as short-term memory (STP), long-term memory (LTP) and STP-to-LTP transition have been well-emulated within N-GOQDs device having a size range of 3 to 6 nm.

2. Experiment

The Ag/N-GOQDs/Pt stacks were fabricated on the thermally oxidized silicon substrate (Si/SiO_2). A Si/SiO_2/Ti/Pt substrate was standard pre-cleaned for 20 min and then dried in N_2 gas. The sized N-GOQDs were solution-prepared from stirring the graphite powder with a solvent for long time (hours), and then solution was heated up to defined temperature to achieve desired size products, i.e. N-GOQDs [7]. For further size separation of QDs different micro-filter membranes (1k, 10k, 50k class) were utilized. Micro-filter membrane of 1k, 10k, and 50 k class could separate different size range of QDs with 0.5 to 3 nm, 3 to 6 nm and 7 to 12 nm, respectively. Later, N-GOQDs quantum dots were drop-casted on the Pt/Ti substrate in concentration of 0.5% in DI water solution to form N-GOQDs thin films on the substrate surface. Later, the Ag top electrode was prepared by sputtering. The I-V electrical characterization was performed by KeySight-1500B analyzer.

3. Results and Discussion

Table I represents the sized N-GOQDs depending on micro-filter membrane class (1k~0.5-3nm, 10k~3-6nm, 50k~7-12nm). The TS characteristic was performed for single, double, and triple-coated QDs and assessed for best performer from 10k-based TS device (marked yellow). **Figure 1a-d** shows the solution drop-casted N-GOQDs to form thin film and its complete device after Ag/N-GOQDs/Pt, following the Ag^+ ions migration mechanism via QDs functional groups, i.e. OH, CO, NH_2, and etc. Optical microscopy (OM) imaging confirms thin films self-assembly abilities of QDs after 70 ºC baking, which are differently sized. **Figure 2a-c** shows I-V TS characteristics of differently sized N-GOQD's devices. TS behavior was observed for each QDs sized device. However, higher V_{th} (~0.8V~0.3V) to induce memory SET operation was observed for 1k- and 50k-sized QDs devices, respectively, and in case of 1k memory switching instabilities. Oppositely, 10k-sized QDs device showed lower V_{th} (~0.17V) switching and better device TS stability, whereas voltage bias applied from 0 V → 0.22 V to induce memory SET operation for on-state (R_{OFF}), controlled by I_{CC}=12μA, and when bias goes back 0.35 V → 0 V, the device's steep self-current decrease observed (back to R_{ON} state), indicating memory RESET operation, and these memory SET/RESET processes is highly repeatable. The important resistance ratio R_{ON}/R_{OFF} is high in order of ~10^6. **Figure 3** displays the pulse voltage operation of the 10k-sized QDs device, which confirms sufficient time to permit spontaneous relaxation of the Ag^+. In this case, one pulse (0.25V and 500μsec) was applied, and the three steps, i.e. "Delay → Shoot → Relaxation" of the TS appear, the inset shows magnified relaxation time, i.e. τ_R~1.5msec. **Figure 4a-d** displays famous biological model of memorization developed by Atkinson and Shiffrin. Interestingly, the bio-synapses follow the same memory model. When stimuli arrive to the synapse, transmitters (triggered by Ca^{2+} ions) conductive channel starts to form inside the synapse and memorize its conductance state for short-time being (short-term memory - STP) and if no further stimuli synapse easily forgets everything. However, upon the many repetitive stimuli, the transition from short-term conductance to long-term conductance can occur and synapse memorizes its conductance state, LTP memorization. In analogy, the 10k-sized Ag/NGOQDs/Pt device after 10 pulses application memorizes elevated conductance state (G~3mS), but after 60 seconds conductance decreased (G~0S). However, after 30 pulses application, the device memorizes elevated conductance state (G~6mS) and even after long time 30 minutes conductance is still measurable (G~5.1mS). Similar to the bio-synapses, the important short-term memory (STP) to long-term memory (LTP) transition could be observed.

4. Conclusions

To date, the TS behavior was demonstrated in differently sized (from ~0.5nm to ~12nm range) QDs Ag/N-GOQDs/Pt stack device, where N-GOQDs thin film serves as memory storage medium. Among all devices, the best TS performance was found in QDs with size range of 3 ~5nm due to thin film conformity. The RS window (R_{ON}/R_{OFF}) was found to be ~10^6 with suitable TS repeatability. The important bio-synaptic functions such as STP, LTP and STP-to-LTP transition were successfully emulated in the artificial electronic synapse device.

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Table I – N-GOQDs Size dependent Threshold Switching (TS) behavior

N-GO QDs Solution-processed Size		1k, 0.5-3nm	10k, 3-6nm	50k, 7-12nm
1 – Single		x - TS	x - TS	x - TS
2 – Double	*Coating with 0.5% N-GO QDs*	o – TS(+/-)	o – TS(++)	o – TS(+/-)
3 – Triple		o – TS(+/-)	o – TS(+/-)	o – TS(+/-)

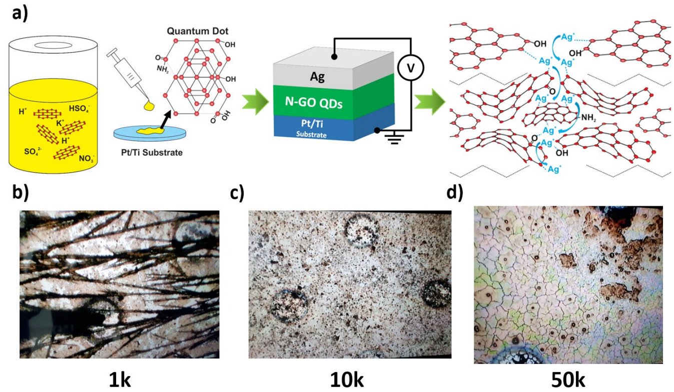

Fig. 1 – **a)** Solution fabricated N-GOQDs and Ag/N-GOQDs/Pt device with I-V set up, **b)** Optical microscopy (OM) image of 1k processed N-GOQDs thin film, **c)** 10k processed N-GOQDs film, and **d)** 50k processed N-GOQDs film.

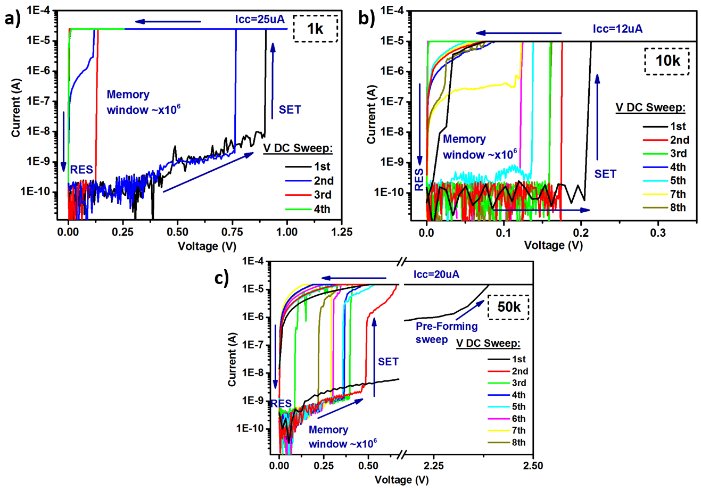

Fig. 2 – Threshold switching (TS) behavior of the Ag/N-GOQDs/Pt devices with **a)** 1k deposited N-GOQDs thin film, **b)** 10k deposited N-GOQDs film, and **c)** 50k deposited N-GOQDs film

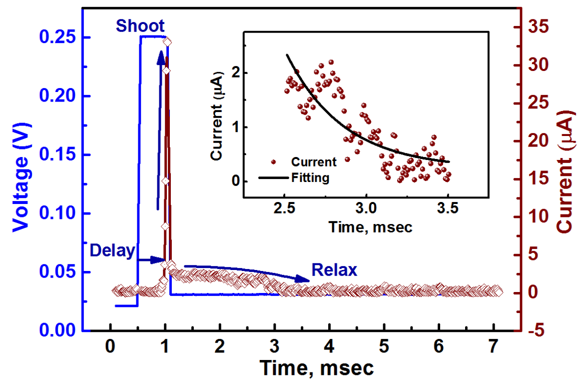

Fig. 3 – Shoot-Delay-Relax pulse characteristics of the Ag/N-GOQDs/Pt for the best TS performer 10k double coated thin film.

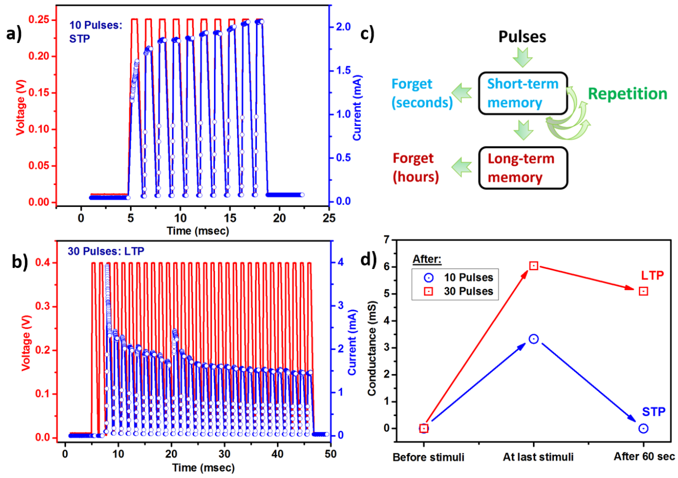

Fig. 4 – **a)** Short-term memory (STP; 10 Pulses) and **b)** Long-term memory (LTP; 30 Pulses) Pulse I-V characteristics of Ag/N-GOQDs/Pt best TS performer (10k) device and according **c)** Atkinson n' Shiffrin memorization model, and **d)** STP & LTP retention of the device after 10 and 30 stimuli, respectively.