Fabrication of Highly Stable Non-Volatile Memory Device Using Plasma-Polymerisation of Hexamethyldisiloxane with Graphene Quantum Dots

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Abstract. We demonstrated the fabrication of a highly stable non-volatile memory (NVM) device using pulsed radiofrequency (rf) plasma polymerization and a simple solution route. The two-terminal NVM devices were fabricated based on a metal-insulator-metal (MIM) structure consisting of graphene quantum dots (GQDs) embedded in hexamethyldisiloxane (HMDSO) dielectric layers. GQDs, the charge trapping layer, and the top contacts were formed by spin coating and spray coating methods. Whereas, the dielectric layers were deposited using pulsed rf plasma polymerization as it is a no thermal stressed induced method to deposit the insulator layers and does not disturb the deposited charge trapping nanoparticles. The current-voltage (I-V) curves showed highly reproducible bistable current behavior with the presence of a hysteresis window when measured at room temperature. The fabricated NVM memory devices were reprogrammable for multiple times with a distinct ON/OFF ratio of 103. Various conduction mechanisms were proposed based on the obtained I-V data.

1. Introduction

In order to realize the optically transparent and mechanically flexible electronics gadgets, the resistive switching polymer-based non-volatile memory (NVM) device is an essential device to be integrated into most of the electronic logic system to provide or store information for logic operation due to its large scale, ease of fabrication, high density, cost-efficient, light-weight, flexible and transparent non-volatile memories production [1-3]. It is common to design the polymer NVM devices in metal-insulator-metal (MIM) structure for resistance switching applications because of its two-terminal simple structure, excellence memory characteristics and high scale-down ability [4, 5]. The spin-coating technique is a preferred method used to deposit the polymer solution dielectric layers for the MIM devices due to its simple automated production process. However, a high heat curing treatment is required after the deposition process and hence induced thermal stress that will cause physical deformation to the device especially the plastic substrate [6]. Therefore, the pulse rf plasma polymerization method to deposit the dielectric layers on indium-tin-oxide (ITO)-coated glass substrate can overcome these drawbacks because heat curing treatment can be avoided after the deposition process.

The deposition of plasma polymerisation produces, at indoor temperature, a highly formed cross-linkage for various types of monomers and ease in control of thickness in obtaining a smooth surface. If the commonly used spin-coating technique was applied in depositing the dielectric layers’ of polymer,
heat treatment is required to achieve a cross-linking structure, but in return, evidently results in physical deformation to the plastic substrate which will obstruct the formation of optically transparent and mechanically adaptable electronic devices [6, 7]. Besides, this approach is reported as an effective way to form an ultrathin film on various substrates to develop new thin gate dielectrics for electronic applications such as humidity sensors, electrical resistors, and optical filters. It is also used to form chemical barrier coatings, anticorrosive surfaces, scratch-resistant coatings, and protective coatings because of its wide selection of monomers, simple processing and low deposition temperature [8-10]. Nevertheless, this useful ability of plasma to polymerize and deposit a solid film from certain organic precursor unintentionally results in poor control of film deposition and hence restricts its applications. Particularly in the traditional continuous wave discharge where the functional groups of precursor gas are seriously dissociated and few reactive moieties can be retained in the deposited film. Hence, it is desirable to seek a method to solve the mentioned problem by tailoring the surface structures of the plasma polymers [10].

Thus, pulsed radio frequency (rf) plasma polymerization can be used to alter the density of the monomer functional groups systematically through controlled variation of the plasma on/off duty cycle. Consequently, functional groups present in the monomer can significantly be retained in the polymerized films and yielded a higher number of nanoparticles to be attached on the surface of the polymerized films during the nanoparticles deposition process [9, 11]. The organosiloxane film also has the potential applications in biocompatible coating for medical implants, perme selective membranes, low dielectric constant inter-level dielectrics in the microcircuits and oxygen barrier coating on polymer for packing [12, 13].

GQDs have improved properties in transparency, adaptability, non-reactive chemicals, low toxicity, and superior functions compared to other nanoparticles. Hence, GQDs has opted as the charge trapping medium inserted in HMDSO layers for the constructed NVM memory devices [14, 15]. In addition, the boundary and quantum confinement effect of GQDs make them a favorable charge trapping medium [16]. The charge trapping medium will be deposited using spin coating method whereas the top contact electrodes of the device could be formed by silver nanowires (AgNWs) using spray-coating technique without going through the costly and time-consuming metal vacuum evaporation process.

2. Experimental Details

GQDs in deionized (DI) water (1 mg/ml) used in this study were purchased from ACS Material. HMDSO monomer with 98.5 % purity (Sigma Aldrich product no: 52630) was purchased from Sigma Aldrich and used without any further purification. Two MIM devices were fabricated with structures of (a) AgNWs/HMDSO/HMDSO/ITO/Glass and (b) AgNWs/HMDSO/GQDs/HMDSO/ITO/Glass, denoted as reference sample and NVM device, respectively, and their schematics are shown in Figures1(a) and 1(b). Inset in Figure 1(b) presents the cross-sectional image performed by scanning electron microscopy (SEM) for NVM device. Prior to device fabrication, the ITO/Glass substrate was cleaned by ultra-sonication sequentially in deionized (DI) water, ethanol and DI water for 20 min, respectively and dried under nitrogen stream. Pulsed rf plasma polymerization of HMDSO was performed on the 1 cm x 1 cm ITO coated glass substrates in a custom-built cylindrical glass chamber, sealed by stainless steel top and bottom plate by viton gaskets. The rf power was supplied by RF generator (RFMN-150, 13.56 MHz) connected to two copper electrodes with impedance matching [17]. The pulse mode was set to 1.0 Vpp with the 2 ms period plasma “high power” time in a 50 % duty cycle and 1.0 ms pulse width in this study. The glass chamber was evacuated by an Edward RV8 pump and the pressure was monitored by a CVM211 stinger vacuum gauge.

Before plasma polymerization of HMDSO, the ITO coated glass substrates were first treated by air plasma for 1 min at 10 W, 25 Pa to any possible trace of contaminants. After the air plasma treatment, the chamber pressure was further evacuated to reach a value of 1.3 Pa. Then, the HMDSO monomer was vaporized into the plasma chamber until it reached a flow rate of 2 sccm. Then, the plasma was ignited by a power of 16 W with 2 ms pulse length at 2 min repetition to obtain the first 20 nm thick HMDSO layer. Next, oxygen plasma treatment was performed for 5 s to reduce the hydrophobicity of
the HMDSO layer, before spin-coating the GQDs at 2000 rpm for 40 s. Afterward, the subsequent HMDSO layer was deposited at 16 W for 2.5 min with the same pulse length to achieve a thickness of 26 nm. It is worth to mention that the thinner dielectric layer deposited adjacent to the ITO electrode is to ensure the ease of charge injection from the ITO electrode whereas the thicker dielectric layer is to yield the higher retention stability for the fabricated device. Finally, the sample on a 100 °C hot plate was spray-coated with AgNWs in isopropyl alcohol (IPA) with the aid of a shadow mask to form 0.5 mm diameter circular top electrodes with an air brush pressurized at 0.1 MPa.

![Diagram of fabricated two-terminal NVM device](image1.png)

**Figure 1.** (1) Schematic cross-sectional structure of the fabricated two-terminal NVM device. (b) FESEM image of the cross-sectional structure for the NVM device.

The current-voltage (I–V) measurements of the fabricated NVM devices were performed at room temperature by using the Keithley 4200-SCS semiconductor characterization system. Bias voltages were applied to the top metal electrode with respect to the ITO electrode for all measurements. The transmittance of the NVM devices was studied by Hitachi UV-VIS Spectrophotometer (U-3900H). ZEISS MERLIN field emission scanning electron microscope (FESEM) was used to obtain the cross-sectional image of the devices.
3. Results and Discussion

Figure 2 shows the study on transmittance in the visible range from 400 to 800 nm transparency for the fabricated MIM devices. The absolute transmittance of the ITO coated glass is varying in the range of 82.0 % to 89.7 %. On the other hand, the reference sample and the NVM device demonstrated a slight drop of absolute transmittance compared to ITO coated glass sample which varies from 81.8 % to 89.6 % and 80.7 % to 89.2 %, respectively, over the visible spectrum. Figure 3 shows the electrical characteristics in a semi-log scale of the fabricated MIM devices. Figure 3(a) shows the $I-V$ measurement of the reference sample with the negligible hysteresis window. Meanwhile, the presence of a significant typical $I-V$ hysteresis window in the NVM device as shown in Figure 3(b) might be attributed to the charge storage capability correlated to the presence of GQDs in the device.

![Figure 2. Absolute transmittance of the reference sample and the NVM device in the visible region.](image)

For both devices, the applied voltage was swept from −2.0 to 2.5 V and vice versa. For the “1st-Sweep” of the NVM device, the applied voltage varied from 0 to -2.0 V. There was an abrupt increase in current at about -0.8 V. It was the “ON” voltage ($V_{on}$) that switched the device from low- to high-current state. It remained at high-current state when the voltage was sweeping from -2.0 to 0 V. Further increase in voltage from 0 to 2.5 V would change the applied polarity on the device. It was noticed that the device switched from high- to low-current state at 2.5 V. The device maintained its low-current state even when the voltage was continued to sweep from 2.5 to 0 V. As a stable and repeatable NVM device is highly desired for real applications, therefore the device was repeatedly scanning the same range of voltage and it was found that the device was able to “write-erase” multiple times and remained distinguishable with $10^3$ ON/OFF ratios as shown in Figure 3(b).

In Figure 3(b), regions I, II, and III was marked in the I–V curves for the “1st-Sweep” NVM device to examine the possible dominant conduction mechanisms at different regions of the device. The plotted curve can be expressed as $I \propto V^n$ and the fitted slope of a double log plot determines the value of the slope, $n$ [16]. It is worth to mention that the occurrence of thermionic emission current conduction at the low voltage region is a commonly observed mechanism related to the thermally generated electrons.
In region I, the electrons could be injected from the ITO electrode and transported over the metal-insulator interface via Schottky and Poole-Frenkel (PF) emissions. The obtained experimental data for the region I as shown in Figure 3(b) is found to obey the relation of \( \ln \left( \frac{I}{T^2} \right) \propto V^{0.5} \) and \( \ln \left( \frac{I}{V} \right) \propto V^{0.5} \), respectively where \( T \) is the temperature, \( V \) is the applied voltage and \( I \) is the current. Those two equations are the Schottky and PF emission mechanisms, respectively. When the voltage was applied to the ITO electrode, a more plausible explanation is that the electrons from the ITO electrode are transported across the HMDSO barrier into the GQDs in a two-step process [12]: the electrons move into the HMDSO layer due to thermionic emission via a field-assisted lowering of the barrier at the ITO-HMDSO interface; then, they move again by PF emission based on the field-enhanced thermal emission of electrons trapped in the HMDSO layer into the GQDs.

**Figure 3.** \( I - V \) characteristics of the (a) reference sample and (b) NVM devices.
In region II, when the voltage is increased to $V_{ON}$, with a fitted slope value of $n \approx 30.5$ ($n \gg 2$) the transportation mechanism starts to follow the common trapped charge-limited current (TCLC) model [19]. Within this region, the presence of GQDs results in the trap sites start to fill up with electrons. This causes an abrupt increase in current. As all the traps are filled, it enters region III where the transport mechanism switches to trap-free space-charge-limited current (SCLC) with $n \approx 2.0$ as predicted by the Lampert–Rose model for SCLC in the bulk [20]. Figure 4 illustrates the possible energy band diagram of the fabricated device being programmed and erased. In the program stage, as shown in Figure 4(a), the -2.0 V pulse applied to the AgNWs electrode will inject electrons from the ITO electrode into GQDs. In the erase stage, as shown in Figure 4(b), the 2.5 V pulse applied to the AgNWs electrode will attempt to eject the trapped electrons out of GQDs. The fabricated device demonstrated the switching behavior similar to a rewritable flash memory.

4. Conclusions

We demonstrated the feasibility of using the pulsed rf plasma polymerization method to fabricate the NVM devices. Plasma polymerization is a thermal stress-free method to deposit the insulator layers. The device fabrication process was completed with the combination of solution-processable techniques to form the charge trapping layer and top metal contacts. The NVM device constructed in MIM structure with GQDs embedded in HMDSO layers and electrical measurement was performed, and a significant typical $I-V$ memory hysteresis window was obtained. The $I-V$ curve fitting suggested that Schottky emission, PF emission, TCLC, and SCLC were identified as the dominant conduction mechanisms through the NVM device. The device shows behavior similar to flash memory and it demonstrated high stability by generating the repeatable hysteresis window with a distinguishable ON/OFF ratio of $10^3$. Therefore, the fabricated two-terminal NVM device using the plasma polymerization method is the right step forward to realize the next-generation flexible and transparent electronic devices.

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