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All-printed and highly stable organic resistive switching device based on graphene quantum dots and polyvinylpyrrolidone composite

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ABSTRACT

We propose all printed and highly stable organic resistive switching device (ORSD) based on graphene quantum dots (G-QDs) and polyvinylpyrrolidone (PVP) composite for non-volatile memory applications. It is fabricated by sandwiching G-QDs/PVP composite between top and bottom silver (Ag) electrodes on a flexible substrate polyethylene terephthalate (PET) at ambient conditions through a cost effective and eco-friendly electro-hydrodynamic (EHD) technique. Thickness of the active layer is measured around 97 nm. The proposed ORSD is fabricated in a 3×3 crossbar array. It operates switching between high resistance state (HRS) and low resistance state (LRS) with OFF/ON ratio ~14 for more than 500 endurance cycles, and retention time for more than 30 days. The switching voltage for set/reset of the devices is ±1.8 V and the bendability down to 8 mm diameter for 1000 cycles are tested. The elemental composition and surface morphology are characterized by XPS, FE-SEM, and microscope.

1. Introduction

Since the physical demonstration of the memristor (a transistor less switch) in 2008 by HP group [1], which was theoretically coined by lean chua in 1974 [2]. Since then, it has extensively researched across the globe for various applications such as non-volatile memories, neuromorphic applications, and digital logic circuits to replace CMOS transistor [2]. CMOS technology is reaching its limits in sense of materials and technology [3]. Memristor's switching behavior gave a realization of analog switch because it provides the same functionality as the transistor does. In the CMOS technology the feature size of the transistor cannot be reduced further either due to the available materials limitations or the fabrication plant limitations [4,5]. However, in the case of a memristor, it provides the freedom of scaling as low as $4F^2$ (where, F is minimum feature size.) [6], therefore the limitation of size and scaling could be possible to overcome with a memristor. Memristor is considering as the next generation memory element for higher integration because of its key features non-volatile nature, small size, easy fabrication and low cost. [7,8]. Performance indices of the memristors are OFF/ON ratio, retention time, switching speed, and current density, which are dependent on the materials used in the memristor for the active layer. To achieve better performance in terms of retention time, stability, switching speed, and power consumption, the investigation of materials for the resistive switching is very important [9–12]. Among the present available materials graphene is the most dominant material for the electronic industry because of its extreme electrical, mechanical, and thermal characteristics [13,14]. Graphene is considering as the future material of electronic industry, and many researchers presented that all the devices and integrated circuits would be fabricated from graphene instead of silicon [15–23]. Especially, graphene quantum dots (G-QDs) are semiconductor nano crystals that they have typically diameter size between 1–20 nanometer (nm) [24]. Due to versatile properties of G-QDs, it is extensively researched for electronic devices [25]. Graphene quantum dots exhibits resistive switching and provide linear resistance at the cost of low resistance during HRS and LRS. Low resistance problem of the graphene QDs can be improve by attaching it with other materials having property of switching [26]. In combination with high resistance material, graphene quantum dots can offer high resistance (during HRS and LRS of resistive switch) and high OFF/ON ratio.

In this paper, we demonstrate a highly stable resistive switching device based on graphene quantum dots and polyvinylpyrrolidone composite (G-QDs/PVP) fabricated on flexible substrate for the first time. The G-QDs and PVP are blended to get the semiconductor property of G-QDs while holding a resistance state (linear)

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and filament conduction property of PVP during transition from one state to another state (switching) in the device. Without PVP, the G-QDs offer low resistance that is not feasible for high dense circuits as electrical power constraint, PVP drastically reduced the current of both states of memristor in this research work. PVP is organic insulator and solvable in number of solvents, here we blend PVP with graphene quantum dots to achieve fully organic active layer. Furthermore, the PVP is fully unified able with G-QDs that help in uniform deposition during EHD. The active layer is sandwiched between top and bottom silver electrodes and forming metal insulator metal (MIM) structure [27]. The fabricated device has morphologically characterized by microscopic images, Scanning electron microscope (SEM) and Focused Ionic Beam (FIB) analysis. The elemental composition characterization is carried out by X-ray photoelectron spectroscopy (XPS). The device has been electrically characterized with the semiconductor analyzer to evaluate the current–voltage (*I*–*V*) characteristics in order to illustrate the memristive behavior. A 3 × 3 crossbar array is demonstrated, and each memristor of the array is accessed randomly through rows and columns without crosstalk. Physical endurance of the device has been tested, after being physically flexed, for flexible electronics applications. The proposed device can be used in flexible resistive stable non-volatile random access memories and can be used in binary switching purposes as well.

For the fabrication of printed electronic devices, a variety of fabrication process is available including atomic layer deposition [28], sputtering [29], sol–gel method [30], anodization [31], roll-to-roll [32], and piezo electric inkjet [33]. Apart from the deposition of high quality insulating layer they have some inherent limitations including high capital cost, high temperature environment, infeasible for mass production, radiation effects on human life and long processing time [34]. Among these processes, electro-hydrodynamic (EHD) method is the best candidate for nano-meter film deposition of continuous drop and atomization types [35]. EHD method is a cost effective, ambient temperature deposition, feasible for prototyping and mass production of printed electronic devices, free of harmful radiation, and rapid fabrication deposition technique [36]. EHD is deployed in the current work to electro-hydrodynamically atomize the G-QDs/PVP composite film and for the silver micro patterned electrodes. No one else has used the said technique and material to show the resistive behavior in the G-QDs/PVP composite layer fabricated through EHD atomization on a flexible substrate. Experimental details are given in Section 2, results and discussions are given in Section 3, and conclusion is summarized in Section 4.

2. Fabrication

Ink for active layer is prepared as: graphene quantum dots (sigma Aldrich) 10 mg is dispersed in 1 ml ethanol, stirred on magnetic stirrer for 2 h and 30 min bath sonicated. Poly(4-vinylphenol) (PVP) (average Mw ~25,000) polymer is dispersed 10% by weight in ethanol and stirred for 1 h on magnetic stirrer. Both inks were prepared separately and then mixed with different ratios to obtain the optimum switching of the device. The best ratio experimentally observed of G-QDs and PVP was 1:1/2. Other mixing ratios resulted in asymmetric threshold voltages, small OFF/ON ratio, and small endurance cycles (see the details for the mixing ratios in the Supporting information material). After mixing the ink with said ratio, it was again stirred with magnetic stirrer for 30 min and 10 min bath sonication prior to use. Ink for silver electrodes is prepared as: Ag nano particle paste sigma Aldrich 55%wt is diluted in 10 ml ethylene glycol solvent mixed for 1 h on magnetic stirrer and then 20 min bath sonication. Ag ink has a surface tension of 24 mN/m, viscosity of 11.3 mPa s, and specific gravity of 1.66 g/ml.

EHD to deposit the electrodes and active layer is done with the help of fabrication facility as shown in Fig. 1a. The setup contains *X*–*Y* stage for the substrate movement, light source and camera to observe EHD con-jet modes, ink storage and supply section, high power voltage source to supply electric potential, nozzle to deposit the thin patterns of electrodes and active layer on the substrate, and computer to monitor and control all the deposition process during the experiment. Substrate was placed on the moving stage; electric potential was applied to the nozzle through the high voltage source and ground to substrate holder. Different modes (dripping, unstable, stable, and multi cone-jet) of atomization were observed as shown in Fig. 1b–e. The proposed devices are fabricated by using a stable cone-jet mode of EHD. Resistive switching devices were fabricated on PET substrate as the layout diagram shown in Fig. 2a. To begin with, bottom silver electrodes (200 μm width) were deposited with the EHD parameters given in Table 1 and cured for 90 min at 120 °C. Composite in of G-QDs/PVP was placed in chamber and pumped to nozzle for the active layer deposition (97 nm thickness), the parameters for EHD atomization during deposition of the active layer are given in Table 1.

For the fabrication of thin patterns for the electrodes of the device, the distance between nozzle and substrate (stand-off) is reduced to 1–3 mm, whereas the distance to deposit the active layer is increased up to 15 mm. Along the stand-off distance the cone jet converts into spray and more area is covered on the substrate resulting in deposition of thin film. In the case of small stand-off distance it covers area almost equal to the diameter of the nozzle and deposits thick film (patterns). After fabrication, sample was cured at 120 °C for 120 min, and then top electrodes were deposited with the same EHD parameters as the bottom electrodes. Contact pads were deposited on the ends of both bottom and top electrodes ends for external circuitry interfacing. After the fabrication and curing process, sample was encapsulated with Al_2O_3 to protect from environmental effects such as oxidation. The fabricated device is shown in Fig. 2b, top and bottom electrodes are

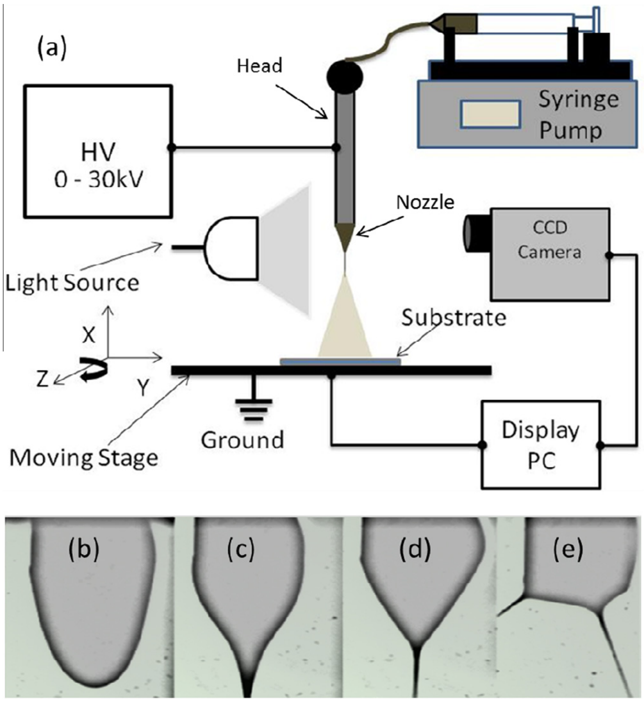

Fig. 1. (a) The EHD schematic diagram. (b) Dripping mode. (c) Unstable jet mode. (d) Stable cone-jet mode. (e) Multi-jet mode.