Journal of Colloid and Interface Science 512 (2018) 767–774

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Digital to analog resistive switching transition induced by graphene buffer layer in strontium titanate based devices

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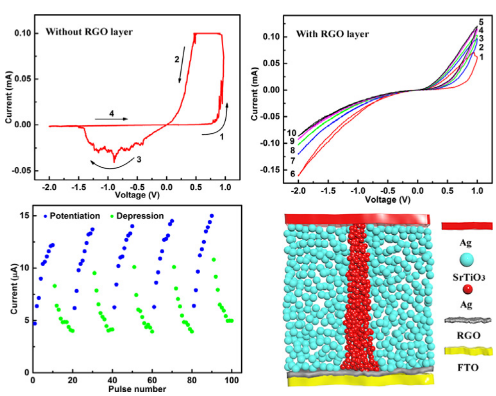
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 August 2017
Revised 27 October 2017
Accepted 31 October 2017
Available online 31 October 2017

Keywords:
Digital resistive switching
Analog resistive switching
Reduced graphene oxide
$SrTiO_3$

ABSTRACT

Resistive switching behaviour can be classified into digital and analog switching based on its abrupt and gradual resistance change characteristics. Realizing the transition from digital to analog switching in the same device is essential for understanding and controlling the performance of the devices with various switching mechanisms. Here, we investigate the resistive switching in a device made with strontium titanate ($SrTiO_3$) nanoparticles using X-ray diffractometry, scanning electron microscopy, Raman spectroscopy, and direct electrical measurements. It is found that the well-known rupture/formation of Ag filaments is responsible for the digital switching in the device with Ag as the top electrode. To modulate the switching performance, we insert a reduced graphene oxide layer between $SrTiO_3$ and the bottom FTO electrode owing to its good barrier property for the diffusion of Ag ions and high out-of-plane resistance. In this case, resistive switching is changed from digital to analog as determined by the modulation of interfacial resistance under applied voltage. Based on that controllable resistance, potentiation and depression behaviours are implemented as well. This study opens up new ways for the design of multifunctional devices which are promising for memory and neuromorphic computing applications.

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https://doi.org/10.1016/j.jcis.2017.10.113
0021-9797/

1. Introduction

Memristors with metal-insulator-metal (MIM) sandwich structures have been widely investigated because of their potential applications in non-volatile memory (NVM), logic operations and neuromorphic computing [1,2]. Resistive switching properties in memristors are closely associated with the change of internal states under external stimuli, such as light, magnetic and electric field. In general, the switching behaviours can be classified into two modes: digital and analog switching [3].

Abrupt change of resistance in digital switching gives rise to the distinguished states, which are beneficial for the information storage. This is ascribed to the formation and rupture of highly conductive filaments between the electrodes caused by migration of oxygen vacancies or active metal ions (Ag^{+}, Cu^{2+}, Ni^{3+}, Al^{3+}, In^{3+}, etc.). Based on a series of characterizations, the evolutions of active metals, oxygen vacancies or oxygen-deficient filaments, have been observed during their switching processes respectively [4–8]. The simultaneous observation of dual-filament consisting of oxygen vacancies and Ag has been also reported very recently [9]. By controlling the filaments growth and dissolution, the low-resistance state (LRS or on state) and high-resistance state (HRS or off state) can be switched easily in the devices. Normally, on/off resistance ratio of more than 10 is needed to realize data storage and low misreading rate [10,11]. Moreover, a relatively high on/off ratio (above 10^{6}) has been reported in many studies, which provides a large memory operation window and facilitates practical memory applications [12,13]. Furthermore, multilevel resistive switching (MRS) devices with as many as 8 states have been fabricated, enabling high-density data storage [14,15].

In contrast to digital switching, analog switching exhibits a gradual change of resistance. This type of switching bears some similarities with the adaptive change of learning state in biological synapses, which are the basic building blocks of a brain and responsible for the learning and memory behaviours [16]. Therefore, a variety of memristors have been investigated to emulate the synaptic functions, including long-term/short-term plasticity (LTP and STP), and spike-time-dependent plasticity (STDP) [17]. These memristive devices acting as artificial synapses can contribute to the realization of artificial neural networks for significantly improving the efficiency of information processing tasks in conventional digital computers.

To better understand the switching mechanisms and improve the performance, many studies have been carried out to implement both digital and analog switching in a same device. By controlling the experimental conditions, the coexistence of both behaviours has been found in several devices, including Ag/$CH_3NH_3PbI_{3-x}Cl_x$/FTO [18], Pt/$BiFeO_3$/Pt [19] and Ag/MoO_{3-x}/FTO [20]. In addition, the transition from digital to analog switching can be induced by varying the electrodes and insulator thickness [21,22]. For digital switching, the random rupture/formation of the filaments usually leads to high variability and low reliability of the devices. An interesting approach to modulate the switching performance consists in deliberately inserting an additional layer in the metal-insulator-metal sandwich to improve the controllability of filaments formation and rupture. For example, the metal oxide layers, such as Al_2O_3 [23], TaO_x [24] and TiO_x [25], have been proposed to improve the switching performance.

Recently, graphene has also been widely employed in memristors as an excellent barrier layer to prevent the penetration of molecules, gases as well as metals (Al, Cu, Ag, etc.). After inserting the graphene, excessive injection of metal ions and filament overgrowth can be effectively suppressed, leading to enhanced performance (e.g., increased uniformity and reliability). By using nanopore graphene layer in the memory device, the filament formation was confined as well [26,27]. As its typical derivatives, graphene oxide (GO) and reduced graphene oxide (RGO) thin films similarly exhibit good barrier function as well [28,29]. Apart from facilitating uniform switching, reduced power consumption owing to the high out-of-plane resistance of graphene has been reported [10,30,31].

Here, the $SrTiO_3$ nanoparticles based memristors have been prepared by a facile solution-based method with using Ag and fluorine doped tin oxide (FTO) coated glass as top and bottom electrode respectively. The $SrTiO_3$ device without GO showed typical digital switching with a small on/off ratio, poor endurance and retention due to random formation/rupture Ag filament and porous structure of $SrTiO_3$ nanoparticles film. However, after inserting the reduced graphene oxide into the $SrTiO_3$/FTO interface, we found that low operational current can be achieved without setting compliance currents. Furthermore, the Ag/$SrTiO_3$/RGO/FTO device exhibited uniform analog switching with good performance; the corresponding synaptic behaviours, including potentiation/depression, were also investigated.

2. Experimental section

2.1. Material synthesis and device fabrication

$SrTiO_3$ nanoparticles were synthesized by a solution-based method at low temperature (80 °C) and were assembled into films by drop-coating based on the previous report [32]. FTO was used as bottom electrode and silver paste with diameter less than 400 μm was selected as top electrode. The final sample Ag/$SrTiO_3$/FTO was dried in oven at 150 °C for 1 h [33]. The Ag/$SrTiO_3$/RGO/FTO device was fabricated under same procedures except that RGO film was firstly formed on FTO glass. In detail, 20 μL of GO solution (1.15 mg/mL) prepared by Hummers method [34] was dropped onto the FTO substrate which was pre-cleaned with ethanol and deionized water, and further treated with ultraviolet radiation for 1 h. After the GO sample was dried, it was sintered in the furnace at 350 °C for 10 min in air to realize the moderate reduction as previously reported [35].

2.2. Characterization and electrical measurement

The crystalline phases of the samples were characterized by X-ray diffractometer with Cu Ka radiation (The PANalytical Xpert Multipurpose X-ray Diffraction System). The cross-section images of the sample were obtained with scanning electron microscopy (FE-SEM, FEI Nova Nano SEM 450). The Raman spectroscopy was measured by an inVia Renishaw Raman microscope excited by a 514 nm laser. The electrical measurements of the samples were carried out using a Keysight b2902a source meter at room temperature.

3. Results and discussion

Fig. 1(a–c) shows the switching characteristics of the Ag/$SrTiO_3$/FTO device with different compliance current (I_{cc}). Upon applying a voltage following the sequence 0 V → 1 V → 0 V → −2 V → 0 V, bipolar switching behaviours are observed. An abrupt change of resistance from HRS to LRS occurs when the positive voltage reaches about 1 V (SET process). We attribute the small set voltage to a large ion flux caused by the large diffusion coefficient of Ag^{+} ions, as it has been shown elsewhere [36,37]. Meanwhile, no forming process is required for the switching behaviours. Subsequent application of negative voltage switches the device back to the HRS (RESET process). Generally, for digital switching, appropriate