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Memristive switching in Cu/Si/Pt cells and its improvement in vacuum environment

Dashan Shang [a,*], Shinbuhm Lee [b], Young Sun [a]

[a] Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Department of Emerging Materials Science, Daegu Gyeongbuk Institute of Science and Technology, Daegu, Republic of Korea

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ABSTRACT

Memristive switching in materials attracts intensive attention due to its potential application for nonvolatile memories. The environmental effect on the switching stability is of crucial importance to the fabrication and performance of a real memory devices. In this work, a solid state electrochemical cell with Cu/Si/Pt sandwich structure has been investigated. The cell shows a forming-free and gradual memristive switching behavior. The environmental atmosphere has significant effect on the switching behavior. We suggest that Cu electrode is oxidized by the atmosphere, forming a CuO_x layer at the Cu/Si interface. The memristive switching can be attributed to the redox reaction between the CuO_x and Si layers with an equilibrium of oxygen exchange between the cell and the environment. By pre-fabricating a CuO_x layer during the cell preparation, the oxygen exchange with the environmental atmosphere is avoided and the switching degradation in vacuum condition is improved. These results provide a fundamental insight into improvement of memristive devices close to a real service condition.

1. Introduction

A simple solid state electrochemical (SSE) cell usually is composed of a solid electrolyte sandwiched by two electrodes. Based on the electrochemical reactions taking place at the electrode/electrolyte interfaces, various kinds of functional devices have been developed, such as fuel cells, batteries, sensors, electrochromic windows, permeation membranes, and so on [1]. Recently, it has been reported that the resistance of some SSE cells can be changed reversibly between high and low resistance states and the resulting resistance states can keep a long time after removing the external electric field [2–4], as has been defined as memristive switching [5]. These properties motivate a new application of the SSE cell as a nonvolatile memory devices, called redox-based resistive switching memory, which has been considered as one of the most promising candidates for next-generation nonvolatile memory devices.

According to the predominant procedure involved in the redox processes, the memristive devices can be classified into two modes [6,7]. One mode is electrochemical metallization mechanism (ECM). Firstly, the active metal, fox example Cu, is used as one of the electrodes and oxidized under the positive bias. Then the Cu^+ ions migrate towards the counter electrode and reduced here to form metal filaments. When the filaments bridge the two electrodes, the cell changes to a low resistance state (LRS). Under the negative bias, the filaments dissolve and break, and then the cell switches to a high resistance state (HRS). The other mode is valence change mechanism (VCM). Similar to the ECM, conductive filaments dominate the resistance switching. However, the filaments are formed by the migration of mobile defects, such as oxygen vacancy, which results in the valence change of metal ions in the electrolyte.

The environmental atmosphere shows important effect on both the ECM- and VCM-mode switching in some SSE cells. For ECM cells, the oxidation of the active electrode is firstly required to generate mobile ions, i.e. $Cu \rightarrow Cu^+ + e^-$, if no mobile ions are included initially in the electrolyte, i.e. $Cu/SiO_2/Pt$ cell [8]. However, the electrode oxidation cannot take place by simply only applying positive bias on it. A counter electrode reaction must proceed, thus supplying counter charge and allowing the injection of cations into the electrolyte to maintain the electroneutrality. Valov et al. firstly found that environmental water molecules were adsorbed in the SiO_2 films and reduced to hydroxyl groups (OH^-) at the counter electrode to provide the counter charges for the Cu anode oxidation [9]. Similar effect has also been observed in $Cu/Ta_2O_5/Pt$ and $Ag/SiO_2/Pt$ cells [10,11], and has been further demonstrated in nanoscale electrochemical reactions [12]. Recently, we have demonstrated that hydroxyl groups created by environmental moisture facilitated the anodic passivation of Ag electrode, causing a VCM switching at the Ag/MoO_{3-x} interface [13]. For VCM cells, usually the oxygen vacancy has pre-existed or electroformed in the solid electrolytic oxides. The oxidation of oxygen ions to oxygen gas is unwanted, because it will cause an exchange of oxygen between the cell and the environment. However, gas bubbles indeed have been observed in some memristive devices [14–16], even though the gas source is still arguable. Yang et al. found that stable memristive switching in WO_3 was observed in oxygen-rich gas and degraded in vacuum and N_2 [17]. Similar results have also been observed by Goux et al. in HfO_2 [18]. Besides that, Messerschmitt et al. demonstrated that the environmental humidity have

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importance impact on the memristive switching behavior in Pt/$SrTiO_{3-\delta}$/Pt cells due to the hydration reaction [19].

From a technological point of view, however, the environment effect makes the cells difficult to use as real memory devices, because it is a challenge to incorporate these environmental factors, such as oxygen gas and/or water molecules, which are incompatible with the present semiconductor fabrication process, into the memory device fabrication and encapsulation. To overcome this disadvantage, a memristive switching cell without environmental impact is highly desired. In this work, we present an investigation on the memristive switching behavior in a Cu-based SSE cell. The cells display a forming-free and gradual memristive switching behaviors, and the switching behaviors show a significant dependence on the environment atmosphere. By prefabricating a CuO layer at the electrode/electrolyte interface, a stable memristive switching in high vacuum condition has been realized, and the corresponding physical mechanism has been discussed.

2. Materials and methods

The Cu/Si/Pt cells were prepared on commercial Pt/Ti/SiO_2/Si wafer substrates by radio-frequency magnetron sputtering at room temperature. Si layers with thickness of 22 nm, 42 nm, 62 nm, and 85 nm were first deposited in an Ar atmosphere of 1 mTorr. Then, Cu and Pt electrodes with thickness of 100 nm and 50 nm, respectively, were deposited on the Si layer in an Ar atmosphere of 5 mTorr. For some samples, a Pt protecting layer of 30 nm was also deposited on the Cu electrode surface. The Cu, Pt, and Pt/Cu electrodes were patterned as square arrays with the size ranging from $25 \times 25\ \mu m^2$ to $125 \times 125\ \mu m^2$ by the photolithography and lift-off technique. The as-deposited Si layer was determined to be amorphous by X-ray diffraction pattern. For comparison, the Pt/CuO_x/Si/Pt cells were also prepared. The CuO_x layer of 30 nm was deposited using Cu target in an Ar/O_2 mixed gas atmosphere of 5 mTorr with Ar:O = 5:1. The current-volatge (*I–V*) characteristics were measured using Keithley 2601 sourcemeter. Electric polarity directed from the top to the bottom electrode was defined as positive. A schematic illustration of the cell structure and the measurement setup are shown in the inset of Fig. 1(a). Because of the two-terminal configuration of our cells, the reference and working electrodes can be seen as the same one. All the measurements were performed on the cells with top electrode size of $75 \times 75\ \mu m^2$ and Si layer of 42 nm at room temperature except when otherwise specified.

3. Results and discussion

Fig. 1(a) shows the typical *I–V* characteristics of the cells with different top electrodes. The voltage sweeps according to 0 V→4 V→0 V→−4 V→0 V at a rate of 0.05 V/s. A current compliance of 100 mA was selected to avoid permanent breakdown. With increasing the positive voltage, the *I–V* curves of the Cu/Si/Pt cell show a sudden increase at $V_{th} = 3.3$ V, and then an obvious hysteresis occurs during sweeping back, indicating a memristive switching behavior from a HRS to a LRS. Under the negative voltage sweep, the cell resistance switches back gradually to the HRS, as signified by the hysteresis direction of the *I–V* curve. With increasing the voltage sweep cycles, as shown in Fig. 1(c) and (d), the *I–V* curves of the Cu/Si/Pt cell gradually shifted to the low current value, especially in the negative voltage region, indicating both the HRS and LRS values of the cell increased with voltage sweep. After about 20 cycles, the *I–V* curves begin to overlap, indicating

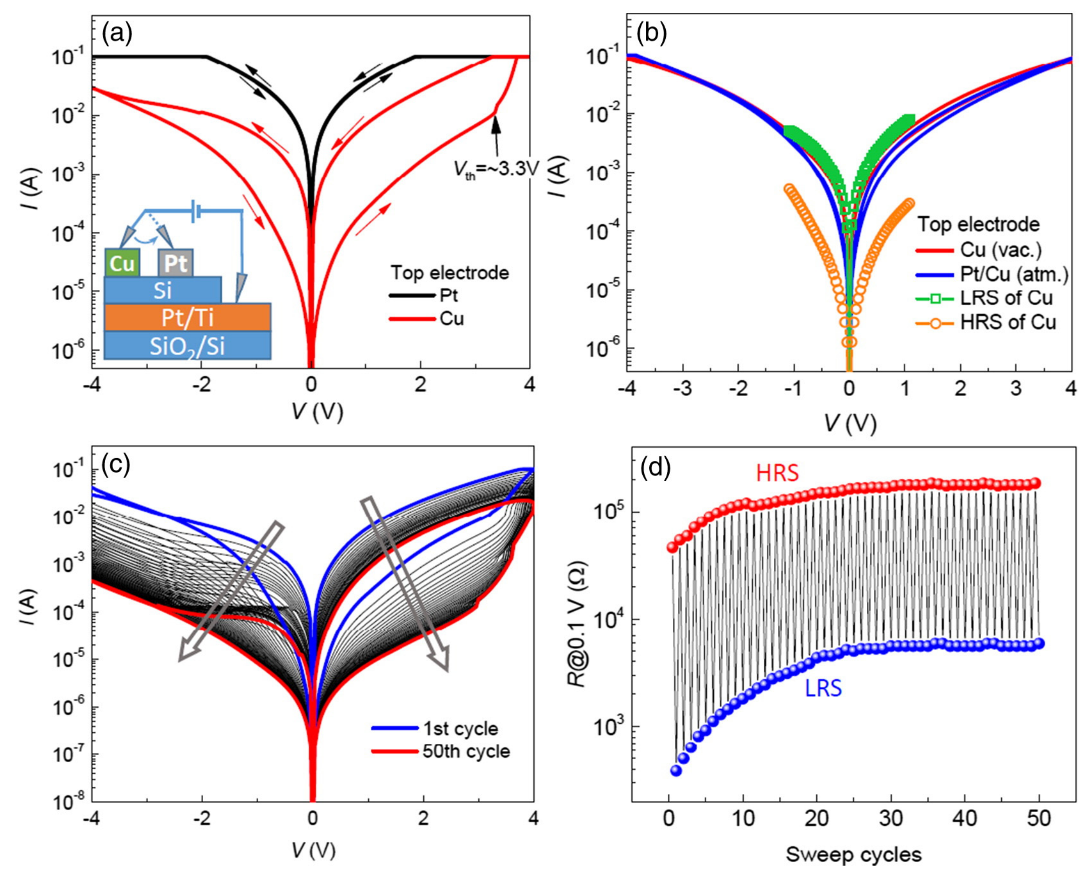

Fig. 1. (a) *I–V* characteristics of the Cu (or Pt)/Si/Pt cells with a current compliance of 100 mA. Inset: schematic of the cell structure and measurement. (b) *I–V* characteristics of the Pt/Cu/Si/Pt cells measured at ambient air condition and the fresh Cu/Si/Pt cells measured under a high vacuum condition ($<3 \times 10^{-5}$ Pa). The Cu/Si/Pt cells was put into a vacuum chamber immediately after the Cu electrode preparation. For comparison, the *I–V* curves of the LRS and HRS of the Cu/Si/Pt cells in (a) were also plotted with voltage sweep range from −1 V to1 V. (c) *I–V* curves of the Cu/Si/Pt cells with 50 cycles of voltage sweep and the corresponding resistance change (d).