Enhanced resistive switching performance in bilayer Pt/TiO$_2$/Co$_3$O$_4$/Pt memory device

Lilan Zou, Jianmei Shao and Dinghua Bao

1 Department of Physics and Optoelectronics, College of Electronics and Information Engineering, Guangdong Ocean University, Zhanjiang 524088, People’s Republic of China
2 State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, People’s Republic of China

E-mail: zoulilan2015@163.com and stsbdh@mail.sysu.edu.cn

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Abstract

In this work, the bilayer Pt/TiO$_2$/Co$_3$O$_4$/Pt and single-layer Pt/TiO$_2$/Pt memory devices were fabricated for investigating their resistive switching characteristics. The statistical switching parameters revealed the enhanced resistive switching performance in the bilayer Pt/TiO$_2$/Co$_3$O$_4$/Pt device, for instance, more centralized operating voltages and current, as well as lower power consumption. The analysis of conductive mechanisms showed that the Schottky emission and Ohmic mechanisms were responsible for the OFF and ON states of the Pt/TiO$_2$/Co$_3$O$_4$/Pt memory devices. The conductive filament mode combined with the fitting results of conductive mechanisms was used to illustrate the resistive switching effect, which provided a microscopic model for a deeper understanding of switching behavior in bilayer devices. Our results indicated that switching properties of TiO$_2$-based resistive random access memory (RRAM) could be improved by inserting a Co$_3$O$_4$ layer.

1. Introduction

Si-based Flash memory has captured the main market because of its enormous application in non-volatile memory field nowadays. However, Flash memory is expected to meet its physical limits with scaling down of microelectronic process nodes. Resistive random access memory (RRAM) represents one of the most promising non-volatile memory in future, due to the advantages of low power consumption, simple structure and fast operation, etc. [1–4] RRAM designing is toward higher performance, larger density and lower consumption, and thus reducing switching power for large scale integrated circuit is necessary. Switching power, as product of the programming current and voltage, is relevant to the device structure, material section and conductive mechanism. Therefore, various materials and novel structure are designed to above goals [5–7]. Transition metal oxides, owing to good compatibility with complementary metal oxide semiconductor (CMOS) process, have been studied for RRAM memory [8–10].

TiO$_2$, one of the most attractive RRAM materials, reveals good resistive switching (RS) properties and has potential application for RRAM, as reported in our previous work [11–13]. However, our research on TiO$_2$-based RRAM still faces great challenges which limits the large-scale application of RRAM. Firstly, the formation of conductive filament (CF) in RS device require a forming process with a high voltage, resulting in inevitably physical damage and the large leakage current. Secondly, the devices suffer from several instable issues on account of the random formation/fracture of the CF. Nowadays, various research approaches, such as the structure optimization and doping, have been attempted to suppress the switching current and improve the uniformity of RRAM [14, 15]. An optional solution is adapting a bilayer structure with engineered oxygen distribution during deposition process [16]. Huang et al has reported the enhanced RS performance of the W/Al$_2$O$_3$/Pt device with a forming free process after inserting an oxygen-deficient AlOx layer [17]. In addition, the uniformity of the bilayer RRAM device can be enhanced because of that the formation/rupture of filament is
limited near the interface of the bilayer film [18–20]. It has also been reported that the switching current of the bilayer HfO2/ZnO memory is suppressed due to interface barrier effect [21]. Co3O4, studied as p-type binary spinel oxide, has attracted considerable attention for the applications in lithium ion battery, electrochemical catalysts and magnetic material due to its excellent electrochemical and magnetic properties. Co3O4 film has also been investigated as RS materials for exploring the RS mechanism in spinel oxide in our reported work, which shows the abundant oxygen defects in the Co3O4 film are responsible for the RS effect with low forming voltage [22]. Hence, these motivate us to research the RS performance of TiO2-based by inserting an oxygen defects-rich Co3O4 layer.

In this study, the bilayer Pt/TiO2/Co3O4/Pt and single-layer Pt/TiO2/Pt devices were fabricated by simple sol-gel method for researching their RS properties. The statistic switching parameters showed that the Pt/TiO2/Co3O4/Pt device exhibited lower switching current and voltages, as well as more stable RS performance. The filament mode combined the analysis of conductive mechanism was employed to elucidate the RS performance. Our results demonstrated that the RS properties of TiO2-based memory device were enhanced by inserting a Co3O4 layer.

2. Experimental procedure

The TiO2/Co3O4 film was prepared by sol-gel method. The Co (CH3COO)2·4H2O and 2-methoxyethanol were used as starting material and co-solvent for synthesizing precursor solution, respectively. And the stoichiometric Co(CH3COO)2·4H2O was added in 2-methoxyethanol (30 ml) to prepare a precursor solution with a concentration of 0.2 mol/L. Next, the Co3O4 film was fabricated on Pt/Ti/SiO2/Si substrates by means of spin-coating process with a rotate speed of 3000 rpm for 20 s, and the amorphous film was obtained after followed baking process at 300 °C for 5 min. The final films were obtained by repeating the fabrication and baking process for several times. Then, the TiO2 film as 2nd RS layer was also fabricated by sol-gel method which was also reported in our previous works [11–13]. The prepared TiO2/Co3O4 film was annealed at 600 °C for 1 h in air ambient, and then the film was naturally cooled to ambient temperature. For comparison and composition analysis, the single TiO2 film and pure Co3O4 film were also prepared in same preparation condition. To form the Pt/TiO2/Co3O4/Pt (BL) and Pt/TiO2/Pt (SL) devices, Pt top electrodes with the diameter of 0.3 mm were prepared on the surface of films by sputtering method.

The scanning probe microscopy (SPM, Bruker dimension fastscan bio) and the field-emission scanning electron microscope (FESEM, JEOL JSM-6330F) were used to observe the surface morphology and cross-sectional view of the film, respectively. The chemical constituents of the film were analyzed by the x-ray photoelectron spectroscopy (XPS, ESCALAB 250). The Keithly 236 sourcemeter connected to a probe station was employed to complete the electrical measurements of the memory in a direct current voltage mode.

3. Results and discussion

Figures 1 (a)–(c) showed the AFM three-dimensional surface images of the single-layer TiO2, pure Co3O4, and bilayer TiO2/Co3O4 films, which indicated the films were smooth with the average roughness of 1.9 nm, 4.0 nm, and 4.6 nm respectively. The cross-sectional view of TiO2/Co3O4 film was depicted in figure 1(d), indicating the thickness of the film was 120 nm and the Co3O4 layer was about 40 nm.

The chemical constituents of pure Co3O4 film were characterized by XPS. Two peaks were observed with the binding energies of 780 eV and 795 eV in the Co 2P spectra of pure Co3O4 film, which indicated the co-existence of Co2+ and Co3+ in the films, as shown in figure 2(a). The obvious peak width between 2p1/2 and 2p3/2 orbits was 15.1 eV, and two weak peaks located at high binding energy region were found in 2p orbits. The Co 2p orbit was consistent with the XPS spectra of Co3O4. In addition, the binding energy backgrounds of 454 eV ~ 468 eV and 527 eV ~ 535 eV were employed to conduct the XPS analysis for Ti 2p and O1s, respectively. The O 1s orbit of pure Co3O4 film could be fitted in two peaks located at 529.8 eV and 531.3 eV, corresponding to the Co-O bonding and the oxygen vacancies (Vo), which was presented in figure 2(b) [23]. Meanwhile, the XPS analysis of Ti 2p orbit for TiO2 layer in TiO2/Co3O4 film was illustrated in figure 2(c). The peaks centered at 458.5 eV and 464.2 eV belonged to the Ti 2p3/2 and Ti 2p1/2, and the spin–orbital splitting energy of 5.7 eV resulted from the anatase TiO2 [24]. The weak peaks located at 458.2 eV and 463.7 eV were attributed to the Ti3+ in the film. The peak ratio of Ti3+/(2p3/2)/Ti4+/(2p1/2) was 14%, indicating the main constituent of the film was TiO2. Similarly, the peaks of Ti-O bonding and Vo in the TiO2 layer were centered at 529.8 eV and 531.3 eV, as exhibited in figure 2(d). The area ratios of Vo peaks of O1 s orbits for pure Co3O4 film and TiO2 layer were 24.8% and 52.7% respectively, and the large number of Vo in Co3O4 film corresponded to the large-size filament in the switching operation [25].
The RS properties of SL and BL devices were investigated by the repetitive I-V curves, which were described in figure 3. Generally, the electroforming process was an essential process to form conductive by generating enough vacancies in switching layers. For single layer RS cells, the repeatable RS property was only obtained after an electroforming process with a high voltage of about $-9 \text{ V}$, which was presented in the inset of figure 3(a). However, the high-voltage forming operation was eliminated in the BL devices. The BL device presented repeated RS cycles after two-step forming process with low forming voltages of $-4.2 \text{ V}$ and $1.2 \text{ V}$, as exhibited in figure 3(b). The BL device switched to low resistive state (LRS) from high resistive state (HRS) with positive operating voltage at set process, while the BL cell switched back to HRS in the reset process with a negative voltage sweeping, and the corresponding threshold voltages were set ($V_{\text{set}}$) and rest voltages ($V_{\text{reset}}$) respectively. In addition, the I-V curves of SL device after forming process were also evaluated. As presented in figure 3(a), the operation current of BL memory was suppressed. The high-voltage forming process was potentially destructive for the device and easily triggered excessive oxygen deficient in the switching layer due to the large electric field, and as a result, brought about larger operating current in SL device $[1–3]$. The figure 3(b) displayed the typical I-V curves of BL memory device, which presented the stable RS performance of BL cell.

To analysis RS performance, the switching parameters of BL and SL devices, including the operation voltages and endurance properties, were investigated, as displayed in figures 4(a) and (b). For BL device, the switching voltages distributed at a relatively lower and more centralized voltage region. Meanwhile, the resistance in HRS and LRS read at 0.2 V of BL device exhibited relatively small variation range. Furthermore, the larger resistance value of HRS and LRS in BL device indicated that the operating current is suppressed. Therefore, the results indicated that the BL structure was a feasible approach for improving the uniformity and reducing the power consumption of the memory device. The retention property of the BL memory was illustrated in figure 5(a), the retention time of the cell was up to 10000 s and the resistance of BL device at 0.2 V exhibited no degradation, which demonstrated the highly nonvolatile characteristics of the BL device. Figure 5(b) showed the statistical distributions of resistance (HRS and LRS read at 0.2 V) and operating voltages in ten samples for the BL and SL devices. The statistical distributions were obtained by randomly selecting ten samples prepared and tested in the

![Figure 1](image-url)

Figure 1. The AFM three-dimensional surface images of (a) single-layer TiO$_2$ film, (b) pure Co$_3$O$_4$ film, and (c) bilayer TiO$_2$/Co$_3$O$_4$ film, which showed the average roughness of 1.9 nm, 4.0 nm and 4.6 nm, respectively. (d) The SEM cross-section view of TiO$_2$/Co$_3$O$_4$ film.
same experimental condition, and the statistical results in BL and SL devices were consistent with the conclusions of figure 4.

To analyze the conducting mechanism of the BL and SL devices, the I-V curves at HRS were fitted with four main transport mechanisms: space charge limited current (SCLC), Fowler-Nordheim, Poole-Frenkel, and Schottky emission behavior. The SCLC was trap-controlled transport mechanism, which contained three regions: Ohmic behavior ($I \sim V$) at low voltage region, Child’s square region ($I \sim V^2$), steep current region ($I \sim V^n, n > 2$) [26, 27]. The Poole-Frenkel was a defect-assisted thermionic emission mechanism with a relation of $\ln(I/V) \sim V^{1/2}$ [28]. The Fowler-Nordheim was interface-limited mechanism where the fitting results of I-V curve obeyed linear relation of $\ln(I/V^2) \sim 1/V$ [29]. The Schottky equation was defined as [30].
Where $A^\ast$ was the Richardson constant, $J$ was the current density, $V$ was the applied voltage, $T$ was the absolute temperature, $k$ was the Boltzmann’s constant, $q$ was the electric charge, $\phi_B$ was the Schottky barrier height, $\varepsilon_i$ was the dielectric constant and $d$ was the Schottky distance.

The Ohmic behavior was the main conductive mechanism at LRS in SL and BL devices due to the linear fitting result of $\ln(I) \sim \ln(V)$, as displayed in figures 6(a) and (b). The Schottky emission mechanisms dominated HRS in SL and BL devices due to the linear relation of $\ln(J) \propto V^{1/2}$, as showed in figures 6(c) and (d). The effective Schottky barrier height could be obtained from the intercept of $\ln(J) \propto V^{1/2}$, the estimated value $\phi_B$ of in BL device was different from that in SL RS cells. The lower Schottky barrier height in SL device was also responsible for the large switching current in HRS and LRS, which probably originated from the excessive defects generated in high-voltage forming process [13]. In addition, the slope of the curve in the BL structure was larger than that in the SL device. The slope of the curve was inversely proportional to the Schottky distance and could be described as: \textit{slope} \propto \sqrt{1/d}$, indicating the Schottky distance decreased in BL devices. The insets in figures 6(c) and (d) showed the corresponding energy band diagrams at HRS in SL and BL devices.

In this work, the well accepted CF mode was adapted to illustrate the RS performance. The CF with the metallic conductivity could be studied as doped region of $V_o$, and the evolution of $V_o$ concentration of CF will lead to RS effect, and the RS effects of BL device was illustrated in figure 7. The bilayer memory was in HRS initially, as illustrated in figure (a). The cell switched to LRS with positive voltage sweeping, which corresponded to the set process. The small-size filament was formed during the first forming process with the voltage of $-4.4$ V, then the filament formed in opposite direction during second forming process with a voltage of 1.2 V. Ultimately, the hourglass-like filament composed of oxygen vacancies made a metallic contact between top and bottom electrodes, as presented in figure 7(b). Forming was an electrochemical reduction process, during which

\[
J \propto A^\ast T^2 \exp \left[ \frac{-q(\phi_B - \sqrt{qV/4\pi\varepsilon_i d})}{kT} \right]
\]
oxygen vacancies were created under high electric fields, as well as enhanced by electrical Joule heating effect [25]. The high-voltage forming process was also potentially destructive and certainly difficult to control with a high electric field applied on the devices. In addition, the high-electric forming process easily triggered excessive oxygen defects and led to large leakage current in the device [1–3]. Therefore, a higher compliance current was required for the single layer Pt/TiO2/Pt device during switching cycles due to the high forming voltage. The low-voltage forming characteristic in bilayer memory could be ascribed to the more oxygen vacancies of Co3O4 film created in fabrication process, which confirmed by the XPS analysis of pure Co3O4 film. The conducting filament ruptured easily at the interface of TiO2/Co3O4 films with a negative voltage sweeping owing to the recombination of oxygen vacancies with oxygen ions, which was also accelerated by Joule heating effect in the film. The Co3O4 layer acted as ‘virtual electrode’ during reset process in the BL devices due to that the large-size filament formed in the second forming process, as illustrated in figure 7(c). Next, the cell switched back to LRS when a positive bias was applied on the device, and the CF at the interface of TiO2/Co3O4 films reconstructed in the process. Combined with the analysis of conduction mechanism above, the decreased Schottky distance and increased Schottky barrier would bring about the smaller operating voltages and low operating current respectively. Therefore, the reduction of operating current and voltage led to more stable RS performance for BL devices. In conclusion, the inserted Co3O4 layer played a crucial role in reducing the switching power and improving RS performance of TiO2-based cell.

4. Conclusions

The BL and SL devices were prepared to investigate their RS properties. The BL devices presented the improved RS characteristics, including more centralized operating voltages and current, as well as better retention performance. The conductive mechanism in the BL devices was studied, which belonged to the Schottky emission and Ohmic mechanisms in HRS and LRS respectively. The filament mode combined with conductive mechanism was used to illustrate the RS properties. Our results indicated that the RS performance of TiO2-based devices was enhanced by inserting a Co3O4 layer.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

There are no conflicts to declare.

ORCID iDs

Lilan Zou https://orcid.org/0000-0002-4381-6224

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