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Structural characteristics and resistive switching properties of thermally prepared TiO_2 thin films

Xun Cao [a,b], Xiaomin Li [a,*], Weidong Yu [a], Yiwen Zhang [a,b], Rui Yang [a,b], Xinjun Liu [a], Jingfang Kong [c], Wenzhong Shen [c]

[a] State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Dingxi Road No. 1295, Shanghai 200050, China
[b] Graduate School of Chinese Academy of Science, Beijing 100039, China
[c] Laboratory of Condensed Matter Spectroscopy and Opto-Electronic Physics, Department of Physics, Shanghai Jiao Tong University, 1954 Hua Shan Road, Shanghai 200030, China

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ABSTRACT

Polycrystalline TiO_2 thin films were formed on Pt(1 1 1)/Ti/SiO_2/Si by thermal oxidation of Ti films with temperatures ranging from 600 °C to 800 °C. Results of Raman spectra testing indicate that the structure of the oxidized TiO_2 films is rutile phase. The resistance switching behaviors (RSB) have been confirmed in Pt/TiO_2/Pt structures. A stable RSB with a narrow dispersion of the resistance states and switching voltages was observed in the sample fabricated with the oxidation temperature of 600 °C. The resistance ratios of high resistance states to low resistance states are larger than 10^3 with the set and reset voltage as low as 2.5 V and 0.6 V, respectively.

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1. Introduction

Recently, the bistable resistive switching of binary transition metal oxides, such as TiO_2 and NiO, has attracted considerable attention due to its potential for nonvolatile resistance random access memory (RRAM) applications [1–5]. The resistance of RRAM is switched from the high resistance state (HRS) to low resistance state (LRS) in the set process, while LRS to HRS in the reset process. Many discussions on the resistance switching mechanism have been intensively carried out based on the filament model [3,6]. But the exact natures of the filaments and the actual mechanism have not been clearly elucidated. In the modern researches, many TiO_2 films are reported being deposited by reactive sputtering or by atom layer deposition (ALD) on conductive substrates to fabricated MIM structures [7–9]. Recently, it is reported that TiO_2 thin films can be easily formed by the thermal oxidation of TiN or Ti layers [10–13]. Compared to other fabrication techniques, the thermal oxidation method is very cost-effective and more compatible with mass-production-level processes. It also has the advantages of simple processing and low cost for practical applications. Therefore, it is of great value to pay more attention to the thermal oxidation technique. However, it is usually not easy to obtain a smooth and dense film due to the diffusion of oxygen in the film. The quality of surface may affect the electric properties of the film. Thus, in order to obtain a high-quality TiO_2 film, more attention should be paid to the process of thermal oxidation. In this report, polycrystalline TiO_2 thin films were fabricated on Pt(1 1 1)/Ti/SiO_2/Si substrates by thermal oxidation of evaporated Ti films. Moreover, the effect of oxidation temperature on the structure properties of TiO_2 films was schematically investigated, and stable resistive switching behavior (RSB) was observed at the oxidation temperature of 600 °C with a narrow dispersion of the resistance states and switching voltages.

2. Experimental

Ti films were deposited on Pt(1 1 1)/Ti/SiO_2/Si substrates by electron beam evaporation at room temperature. During the Ti metal evaporation, the pressure inside the chamber was maintained at 2×10^{-4} Pa. Then about 200 nm thick polycrystalline TiO_2 thin films were produced by thermal oxidation of the as-grown Ti films with temperature ranging from 600 °C to 800 °C for 30 min in a tube furnace. The oxygen flow rate was fixed at about 30 cm^{-3} min^{-1} and the prepared TiO_2 films were marked as T-600, T-700, and T-800, respectively. For the electrical measurement, Pt top electrodes of 100 μm in diameter were fabricated using electron beam evaporation with a metal shadow mask at room temperature.

Current–voltage characteristics were examined by Keithley 2410c source meter unit. During the electrical measurements, the bias voltage was applied on the Pt top electrode while the Pt bottom electrode was grounded. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to characterize the surface morphology of as-prepared films. Raman spectroscopy measurement was used to investigate the structure of the TiO_2 films.

* Corresponding author. Tel.: +86 21 52412554; fax: +86 21 52413122.
E-mail address: lixm@mail.sic.ac.cn (X. Li).

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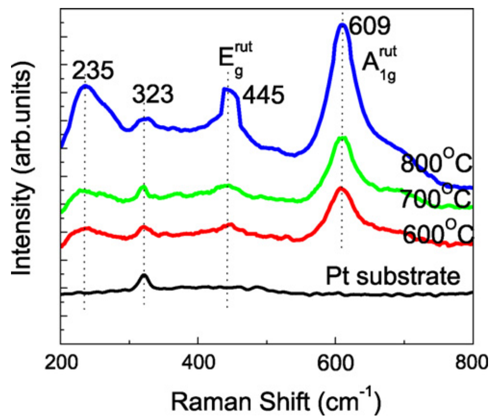

Fig. 1. Raman spectra of TiO_2 films formed on Pt(1 1 1)/Ti/SiO_2/Si substrates by thermal oxidation at 600 °C, 700 °C and 800 °C.

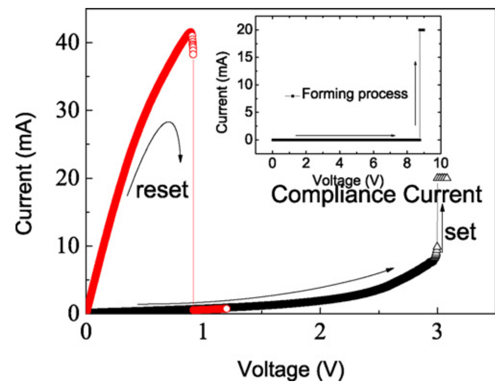

Fig. 3. Typical *I*–*V* curves of Pt/TiO_2/Pt structure with CC of 20 mA. The inset displays forming process under a high electrical stress.

3. Results and discussion

The XRD patterns show that the TiO_2 films are polycrystalline. However, some important peaks which are hidden in the case of Pt/Ti/SiO_2/Si substrates can only be ambiguously observed from XRD result [11]. In contrast, the Raman spectra clearly reveal the phase composition in the TiO_2 films, as shown in Fig. 1. In the Raman spectra, the band located at 445 cm^{-1} is assigned to the E_g modes, and the band located at 609 cm^{-1} to the A_{1g} mode of rutile TiO_2. These values are in good agreement with bulk rutile with E_g at 447 cm^{-1} and A_{1g} at 612 cm^{-1} [14,15]. In addition, an extremely weak peak of TiO_2 films located at ~235 cm^{-1} is attributed to a combination of several modes [16]. And the peak located at ~323 cm^{-1} is ascribed to the effects of the substrates. Thus, the prepared TiO_2 should be predominant in the polycrystalline rutile phase. With the increase of oxidation temperature, the peaks of rutile phase become stronger, which indicates the increase of the crystallinity of the formed TiO_2 films.

Fig. 2 illustrates the morphology evolution of the films oxidized at different temperature. From the SEM image, it can be seen that the average grain size of the Ti film presented in Fig. 2(a) is several nanometers prior to oxidation. With increasing thermal oxidation temperature, the surface become rough and the nano-sized crystalline grains appear. While the microstructures of the T-600 are relatively homogeneous in comparison to T-700 and

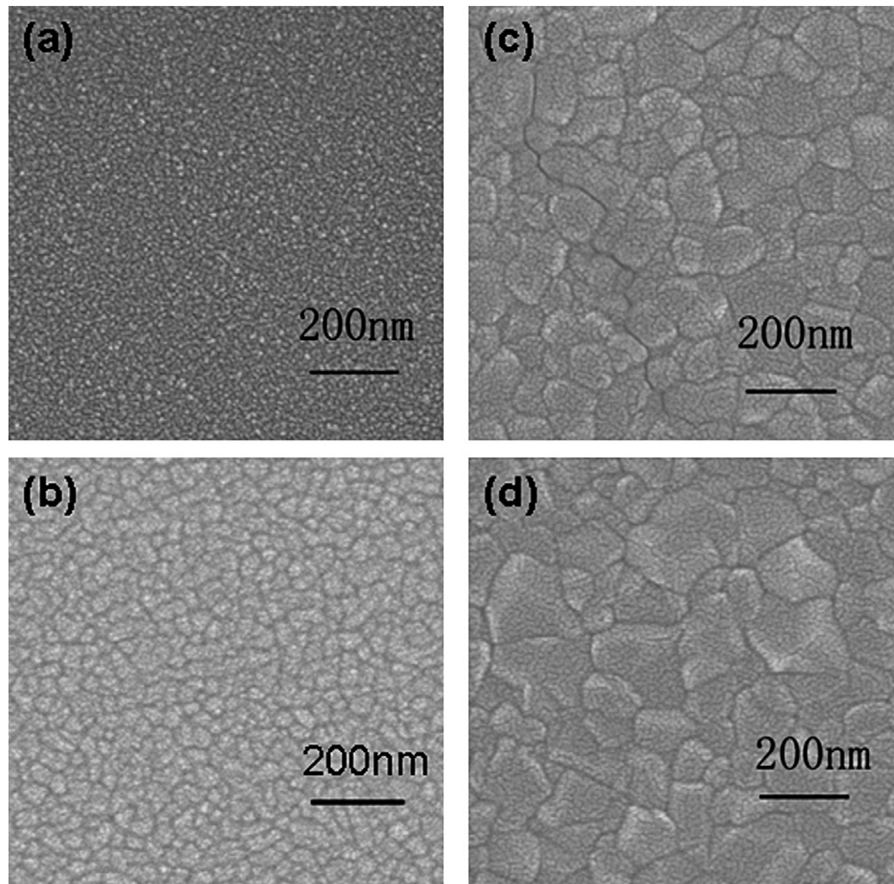

Fig. 2. Morphology evolution of (a) as-deposited Ti film, and following oxidation at (b) 600 °C, (c) 700 °C and (d) 800 °C.

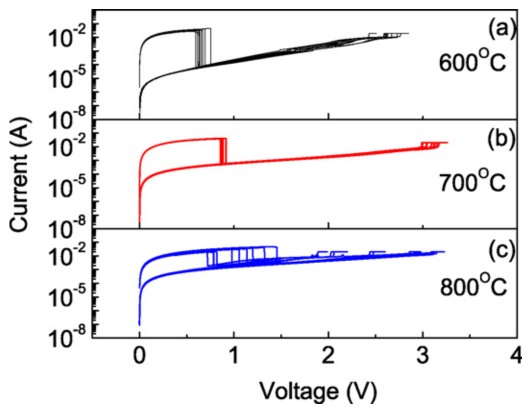

Fig. 4. Current vs voltage characteristics of Pt/TiO_2/Pt structures with TiO_2 oxidized at (a) 600 °C, (b) 700 °C and (c) 800 °C.

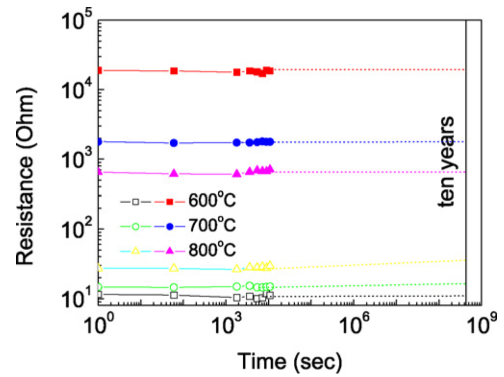

Fig. 6. Data retention characteristics of the fabricated Pt/TiO_2/Pt structures with TiO_2 oxidized at different temperatures. The extrapolation method is employed to give a long-term prediction result.

T-800 (where some large grains can be seen), as illustrated in Fig. 2(b)–(d). In addition, the result of AFM measurement shows that the roughness of T-600, T-700, and T-800 are 7.35 nm, 8.24 nm, and 9.26 nm, respectively (referred AFM photo are not shown here).

To confirm the switching characteristics of T-600 TiO_2 films, the typical current–voltage (I–V) curves are obtained, as shown in Fig. 3. A high electrical stress with a current compliance of 20 mA is necessary to initiate the switching behavior of the Pt/TiO_2/Pt structures, which is known as the forming process, as illustrated in the inset of Fig. 3. After the forming process, the device is in the LRS. Then, by sweeping the voltage from zero to a certain value (the reset voltage), current suddenly drops and the resistance of the device switches to the HRS. While sweeping again, an abrupt jump of current appears at a specific voltage (the set voltage), which is always larger than the reset voltage. The resistance switches to the LRS again. It is noticed that compliance current was required to protect the sample from a permanent breakdown during the set process (from HRS to LRS).

The switching characteristics of the sample T-600, T-700, and T-800 are shown in Fig. 4. The forming voltage values for T-600, T-700 and T-800 are 8.3 V, 7.6 V, and 6.2 V, respectively. The average values of the set/reset voltage (V_{set}/V_{reset}) do not show significant dependence on the oxidation temperature. However, the fluctuations of V_{set} and V_{reset} for the T-600 and T-700 grown sample are smaller in comparison to T-800. While the set and reset voltage for the T-600 is 2.5 V and 0.6 V, respectively, which is lower than the other two samples. To evaluate the reliability characteristic, repeated switching cycling tests are attempted. The on-/off-state resistances with different thermal temperatures are shown in Fig. 5. The ratios between the HRS (off-state) and the LRS (on-state) decrease, when the oxidizing temperature varies from 600 °C to 800 °C, which may be ascribed to the decrease of the resistance due to oxygen deficiency at a higher oxidation temperature.

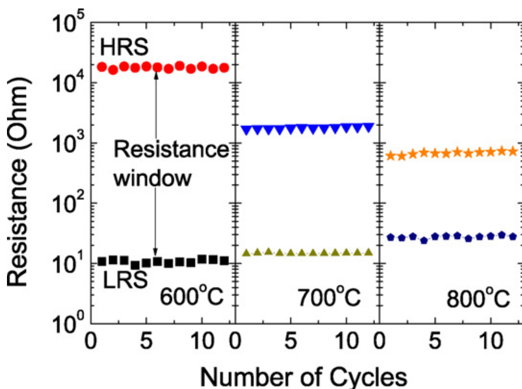

Fig. 5. R_{on} and R_{off} dispersions for Pt/TiO_2/Pt according to switching cycles with different thermal temperatures. R_{on} and R_{off} are measured at V = 0.1 V.

The resistance switching has been reported to be closely related to the formation and rupture of conducting filaments which are formed by percolation of some kind of defects [17,18]. In TiO_2, the most probable defects are Ti interstitials (Ti_i^{4+}) or oxygen vacancies ($V_{O^{2+}}$). As the oxidation temperature increases, the initial resistance of the sample T-600, T-700 and T-800 decreases from about 10^8 Ω to 10^6 Ω, indicating that more defects appear at high temperature. Based on the Raman and SEM data, it is suggested that the crystallinity and microstructure of the films may be highly relevant to the defects in TiO_2 films. The results show that the film with a homogeneous microstructure and low crystallinity exhibits stable and uniform RSB. Moreover, because the TiO_2 thin films in this study have polycrystalline structure, the grain boundaries may also make a considerable contribution to the easy formation of the conductive filament and the stable resistive switching. With the increase of oxidation temperature, the crystalline grains become larger resulting in less grain boundaries, which may be a possible reason for the decrease of HRS, as shown in Fig. 5. However, the exact mechanisms of the resistive switching of TiO_2-based memory devices are not fully clear at the present and further studies are needed to reveal the physical natures.

The data retention characteristics of the fabricated Pt/TiO_2/Pt structures in HRS and LRS are also measured. As shown in Fig. 6, no significant changes of resistance magnitudes in HRS and LRS are observed after the duration at room temperature for 10^4 s, which are projected to demonstrated 10-year retention with nondestructive read-out under room temperature. The superior data retention characteristics of the Pt/TiO_2/Pt structures reveal the potential for nonvolatile memory applications.

4. Conclusions

The structural characteristics and resistive switching properties of the Pt/TiO_2/Pt structures were investigated, in which the rutile-phase TiO_2 thin films were prepared by thermal oxidation. These structures exhibited reproducible resistance switching during I–V measurements. Results show that the film oxidized at 600 °C has a narrow dispersion of the resistance states and switching voltages with the resistance ratios larger than 10^3. It is suggested that a stable and uniform resistance switching behavior can be obtained by controlling the microstructure and the concentration of defects in the TiO_2 films.

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