



## Research paper

Effect of anodic oxidation time on resistive switching memory behavior based on amorphous TiO<sub>2</sub> thin films device

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## ABSTRACT

Resistance random access memory (RRAM) is a promising memory technology in the applications of memory device. Herein, the amorphous TiO<sub>2</sub> thin film was grown onto titanium (Ti) foil by anodic oxidation. Further, the Ag/TiO<sub>2</sub>/Ti sandwich structure device was prepared, which displays a resistive switching memory effect with a high HRS/LRS resistance ratio with ~27 at room temperature when the TiO<sub>2</sub> film was oxidized ~5 min. Finally, the formation/rupture models of Ag conductive filaments are suggested to explain the resistive switching memory behavior. This work open a new way for preparing the RRAM device for memory applications in the future.

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## 1. Introduction

At the information age, the storage means of information is particularly important. The research of RRAM has received great attention after the presenting concept of memory effect in 2000 [1]. In 2008, Strukov et al. demonstrated the existence of resistive switching memories through theoretical research [2]. Compared to conventional memory, RRAM has been considered as potential candidate for future memory device with the advantages of its higher integration density and faster storage speed [3–7]. Studies have shown that many materials have resistive switching memory effects, for example metal oxides, organic matter, biomaterials, etc. [8–15]. The oxide semiconductor has attracted more attention because it has a relatively simple preparation process, and it is easy to control the composition of the film [16–20].

Recently, TiO<sub>2</sub> also attracts attention for using in memristor fabrication [21–23]. The TiO<sub>2</sub> film has the advantages of simple preparation technology, convenient operation, good-stability and

so on. The article reported that direct growth of nanotubes on transparent substrates exhibits stable bipolar resistive switching behavior [24], indicating that the stable resistive switching effect originate from the existence of conducting filaments along the walls of the TiO<sub>2</sub> nanotube. In addition, the TiO<sub>2</sub> nanostructure was synthesized by different method, for example, the amorphous TiO<sub>2</sub> thin film can be synthesized by atomic layer deposition [25–29], Sahu et al. reported the resistive switching mechanism of TiO<sub>2</sub> grown by atomic layer deposition (ALD) [30], it represented the transient characteristics of Au/TiO<sub>2</sub>/Pt resistive switching device with fast switching times, which can be achieved in this TiO<sub>2</sub> thin films. These methods are all-expensive and need stricter conditions like high temperature or vacuum. We list the resistive switching characterizes based on TiO<sub>2</sub> devices in the Table 1, it can be seen that the resistance ratio is not very large by chemical method in many previous works.

In this work, we explored the fabrication of TiO<sub>2</sub> on Ti foil by one-step electrochemical anodization, which is simple and low cost process. Further, the Ag/TiO<sub>2</sub>/Ti sandwich structure device was prepared, which displays a resistive switching memory effect at room temperature when the TiO<sub>2</sub> film was oxidized ~5 min. In particular, the effects of various oxidation time on resistive switching memory behavior are studied. Finally, the resistive switching

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**Table 1**The resistive switching characterizes based on  $\text{TiO}_2$  devices.

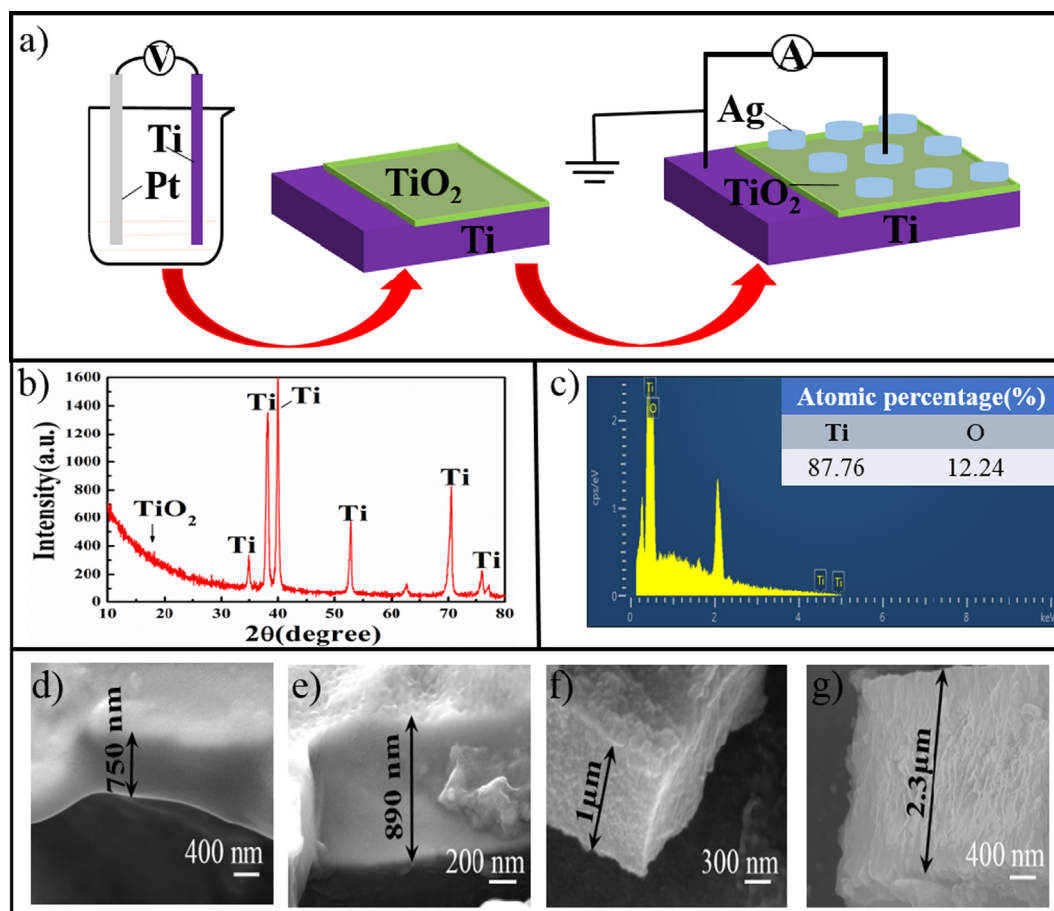
Device	Fabrication method	Ratio	Endurance	Ref.
Cu/ $\text{TiO}_2$ (nanotube)/Pt	Electrodeposition, plasmar sputter	14	20	[16]
Pt/PAA/ $\text{TiO}_2$ (nanotube)-ann/Ti	Anodization, PECVD	4	40	
Pt/PAA/ $\text{TiO}_2$ (nanotube)/Ti	Anodization	5	20	[17]
Pt/PAA/ $\text{TiO}_2$ (nanotube)-ann/Ti	Anodization, PECVD	4	40	
Pt/PAA/ $\text{TiO}_2$ (nanotube)/Ti	Anodization	5	20	[24]
Au/ $\text{TiO}_2$ /Pt	ALD	$10^2$	1000	[30]
Ag/ $\text{TiO}_2$ /Ti	Anodization	27	16	*

memory behavior is explained by the formation/rupture model of Ag conductive filament. Our procedure for fabrication of the nanodevice can be usefully for producing many other different materials to the next generation nanodevice technology.

## 2. Experiment

In our experiment, titanium foils ( $2\text{ cm} \times 3\text{ cm} \times 1\text{ mm}$ ) were used as substrates for anodic growth of  $\text{TiO}_2$  thin films. After grinding and leveling the Ti foil, we cleaned it by ultrasonic with acetone solution, rinsed in ethanol and dried. A two-electrode system was used in anodization process while the platinum as the counter electrode and Ti foil as the work electrode. The electrolyte containing 0.25 wt%  $\text{NH}_4\text{F}$  and ethylene glycol, the constant voltage of 60 V is applied by a DC power while continuously stirring. The distance between two electrodes is  $\sim 2\text{ cm}$ . Samples are anodized for 1, 3, 5, 10 min respectively. The underlying Ti foil was used as the bottom electrode

(BE) in the resistive switching devices, after that we drop the several drops of silver on the film as top electrode (TE) and the thickness is about 1 mm. These samples would be referred to as S1, S3, S5 and S10, where “S” refers to the sample. Fig. 1a shows the schematic of fabrication of Ag/ $\text{TiO}_2$ /Ti. Next, the morphology, cross section and energy spectrum of titanium dioxide thin films was measured by scanning electron microscope (SEM), and their X-ray powder diffraction (XRD) pattern were also measured. The current-voltage (I-V) curves of Ag/ $\text{TiO}_2$ /Ti device and Au/ $\text{TiO}_2$ /Ti were measured by an electrochemical workstation. Field-induce surface photovoltage measurements were carried out with a self-assembly SPV test system based on the lock-in amplifier (SR830-DSP) to identify the separation characteristics of photo-generated charge carriers. In the photovoltaic cell, a glass substrate covered with indium tin oxide (ITO) was used for the top electrode, and amorphous  $\text{TiO}_2$  film on Ti foil acted as the bottom electrode. All measurements were conducted under ambient conditions at room temperature [31].



**Fig. 1.** (a) The preparation process of resistive switching memory device. (b) XRD spectra of the  $\text{TiO}_2$  thin film. (c) EDX spectrum of  $\text{TiO}_2$  thin film. (d → g) The cross sectional SEM image of as-prepared  $\text{TiO}_2$  thin film which oxidation 1, 3, 5, 10 min, respectively.

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