Research Article
Deposition-Parameter-Determined Resistive Switching Characteristics in TiO$_{x}$/Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ Bilayers

Xiaoyu Zhou, Yuan Luo, Aidong Li and Di Wu

1National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
2Department of Materials Science and Engineering, College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China
3Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

Correspondence should be addressed to Di Wu; diwu@nju.edu.cn

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Abstract

Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT) ferroelectric thin films were deposited epitaxially, by pulsed laser deposition, on (001) SrTiO$_3$ substrates buffered with La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) electrodes. Amorphous TiO$_x$ thin films were deposited on top of PZT at various temperatures and oxygen chamber pressures. Bipolar resistive switching characteristics of Pt/TiO$_x$/PZT/LSMO heterostructures are found to vary with TiO$_x$ deposition parameters, from an interface controlled ferroelectric diode behavior to a bulk-controlled conductive filament behavior. The observations are discussed in terms of the concentration and migration of oxygen vacancies in the TiO$_x$ layer.

1. Introduction

Although memories based on FLASH techniques are ubiquitous nowadays, novel nonvolatile memories, such as phase-change memories, resistive switching memories, and magnetic and ferroelectric tunnel-junction-memories, have attracted much attention recently to achieve lower power consumption and higher data storage density. Among these emerging memories proposed, resistive switching memories have shown advantages such as scalability [1, 2], high speed [3], long data retention, high-endurance [4], and low energy consumption [5].

Resistive switching behaviors have been reported in a number of materials due to various mechanisms. In binary transition metal oxides, resistive switching has been extensively studied and modulations on filamentary conduction have been widely accepted. Formation and rupture of conductive TaO$_{1-x}$ filaments, responsible for resistive switching in Pt/SiO$_2$/a-Ta$_2$O$_5$/a-TaO$_{2-x}$/Pt heterostructures, have been directly observed by transmission electron microscopy [6]. Salaoru et al. and Bousoulas et al. proposed that concentration and distribution of oxygen vacancies have a great impact on the diameter of the conducting filaments and hence the operation of TiO$_{2-x}$-based memory devices [7, 8]. However, other resistive switching mechanisms have also been proposed. For example, resistive switching in ZrO$_2$ has been ascribed to space charge limited currents modulated by Zr$^+$ traps [9]. Electrically induced modulations on oxide/electrode interface barriers may also result in resistive switching [10, 11]. Although such modulations can be achieved through electric-field-driven migrations of charged defects, ferroelectric switching provides a unique modulation mechanism in this respect, the switchable ferroelectric diode behavior, as first observed in BiFeO$_3$-based devices [12, 13]. In these devices, Schottky barriers are formed at both interfaces and the barrier heights can be switched to a high or a low level as a response to the switched bound charges at the interface due to ferroelectric switching.

In this report, we show that resistive switching in Pt/Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT)/Pt devices can be tuned from a ferroelectric diode behavior to an oxygen vacancy controlled behavior by inserting a TiO$_x$ interfacial layer between PZT and Pt top electrodes. Deposition parameters of the TiO$_x$ interfacial layer, such as substrate temperature and oxygen chamber pressure, are demonstrated significant to the observed resistive switching behavior.
2. Experimental Section

The heterostructures studied were deposited by pulsed laser deposition (Adnano Corp.). A Coherent CompexPro 205F KrF excimer laser was employed, with an output of 248 nm at 2.0 Hz repetition. The energy flux was estimated as 1.0 J/cm$^2$ for all the depositions. La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) electrodes were deposited epitaxially on (001) SrTiO$_3$ (STO) single-crystal substrates at 800°C. Then Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT) were deposited on top of LSMO at 650°C. For both LSMO and PZT depositions, the oxygen partial pressure was kept at 13.3 Pa. TiO$_x$ films were deposited either in background vacuum (10$^{-5}$ Pa) or in 2.0 Pa oxygen pressure at various temperatures from 30 to 300°C. The thicknesses of LSMO, PZT, and TiO$_x$ layers are 40, 50, and 50 nm, respectively, as calibrated using a Zeiss Ultra 55 field emission scanning electron microscope. For electrical measurements, Pt top electrodes, 100 µm in diameter, were sputter-deposited through a shadow mask.

Crystal structures of the multilayers were characterized by X-ray diffraction (XRD) using a Rigaku ULTIMA-III diffractometer with a Cu Kα radiation. Surface topography was studied using an Asylum Research Cypher atomic force microscope (AFM) in contact mode. Electrical measurements were conducted using a Keithley 2400 source-measure unit. Voltage was applied to the Pt top electrodes and the bottom LSMO electrodes were always grounded. Chemical analysis was carried out ex situ by X-ray photoelectron spectroscopy (XPS) using a Thermo Fisher K-Alpha spectrometer equipped with an Al Kα (1486.7 eV) X-ray source.

3. Results and Discussion

Figure 1(a) shows XRD patterns of TiO$_x$/PZT/LSMO heterostructures deposited on (001) STO substrates. The TiO$_x$ layers were deposited in 2.0 Pa oxygen at various temperatures from 30 to 300°C. Only diffraction peaks from (001) crystalline planes of PZT and LSMO are observed,
Figure 2: *I-V* curves of Pt/PZT/LSMO (a), Pt/TiO$_x$/PZT/LSMO in which the TiO$_x$ layer is deposited at 30 (b), 80 (c), 150 (d), and 300°C (e) in 2.0 Pa oxygen pressure and Pt/TiO$_x$/LSMO in which the TiO$_x$ layer is deposited at 30°C in 2.0 Pa oxygen pressure (f). The arrows indicate the voltage sweeping directions. The inset in (b) shows the *I-V* curves measured after the PZT layer is poled to opposite directions.
accompanied with peaks from the substrate. This indicates that PZT and LSMO are grown coherently to the STO substrates and the TiO$_x$ films are amorphous. The c-axis lattice parameter of PZT, obtained from the XRD patterns, is 4.090 Å, greater than its bulk value 4.082 Å. This can be ascribed to the in-plane epitaxial strain exerted by the LSMO layer underneath. Amorphous TiO$_x$ is a result of low deposition temperature [14]. Surface morphology of the samples was checked by AFM. All the samples show a smooth surface, with a root-mean-square roughness less than 3.0 Å. A representative example is shown in Figure 1(b), where the top TiO$_x$ layer was deposited at 80°C in 2.0 Pa oxygen. Figure 1(c) shows the ferroelectric hysteresis loop of a 50 nm PZT film. The coercive voltage is about 3.0 V and the remnant polarization is about 40 μC/cm$^2$, in agreement with those reported in the literature [15, 16].

Current-voltage (I-V) characteristics of Pt/PZT/LSMO heterostructures are shown in Figure 2(a). The voltage was set to sweep from 0 V to 10.0 V, then from 10.0 V to −10.0 V, and finally from −10.0 V back to 0 V. Pronounced bipolar resistive switching can be observed. The device is initially in the high resistance (low current) state. It is switched to a low resistance (high current) state when the voltage exceeds about 3.2 V. When negative voltages are applied, the device behaves in a similar way, switching from the high resistance state to the low resistance state at about −3.4 V. Note that the resistance state switches at the coercive voltage of the PZT film. Figures 2(b)–2(e) show I-V curves of Pt/TiO$_x$/PZT/LSMO heterostructures, in which the TiO$_x$ layer was deposited at various temperatures in 2.0 Pa oxygen. In Figure 2(b), when the TiO$_x$ layer is deposited at 30°C, the resistance switching behavior of Pt/TiO$_x$/PZT/LSMO is similar to that of Pt/PZT/LSMO. The inset of Figure 2(b) shows the I-V curves of the same device, measured after poling the PZT layer by a 10.0 or a −10.0 V pulse. Rectifying characteristics, switched by the poling voltage, are observed. This is a typical ferroelectric diode behavior, in which the resistance, read by a certain positive or negative voltage, is controlled by the polarization direction in the ferroelectric layer [17, 18]. However, the resistance switching behavior varies with the increase of TiO$_x$ deposition temperature. When the TiO$_x$ deposition temperature is above 150°C, the device exhibits an initial low resistance state, which can be switched into a high resistance state when the voltage exceeds 6.8 V. This high resistance state can be maintained until a negative voltage stronger than −5.5 V is applied, at which the device is reset to the low resistance state. Similar resistance switching sequence is observed in Pt/TiO$_x$/LSMO heterostructures, as shown in Figure 2(f). This is typical for bipolar resistance switching observed in NiO, Ta$_2$O$_5$ and TiO$_2$ [19–21], which is ascribed to the formation and rupture of conductive filaments [6].

These observations indicate an evolution of the resistive switching behavior from an interface controlled to a bulk-controlled mechanism, by increasing the deposition temperature of TiO$_x$ layers. It has been reported, in TiO$_x$ films, that oxygen deficiency might be enhanced at elevated deposition temperatures [22]. Therefore, the conductive filaments in TiO$_x$/PZT heterostructures may probably be formed by oxygen vacancies. In heterostructures where the TiO$_x$ layers are deposited at 30 and 80°C, the initial high resistance state may be a result of the highly resistive PZT layer. With increasing TiO$_x$ deposition temperature, the concentration of oxygen vacancies increases. These charged defects may diffuse into PZT during deposition and form the conductive filaments. Therefore, the initial state becomes a low resistance state. When a positive voltage is applied, more oxygen vacancies are driven into PZT and the diameter of the filaments may grow. However, Joule heating at positive high voltages may fuse the conductive filaments and set the device into a high resistance state.

Figure 3: I-V curves of Pt/TiO$_x$/PZT/LSMO in which the TiO$_x$ layer is deposited at 30 (a) and 150°C (b) in background vacuum.
Figure 4: XPS spectra of Ti_{2p} photoemissions in TiO_x deposited at 30° C (a, d), 80° C (b, e), and 150° C (c, f) in 2.0 Pa oxygen pressure (a–c) and in background vacuum (d–f).
To check the assumption that the observed resistance switching behavior is associated with oxygen vacancies in TiO$_x$$_2$O$_{5–x}$/TaO$_{2–x}$ heterostructures, we studied the valence states of Ti ions in TiO$_x$. Photoelectron spectra emitted from Ti$_{2p}$ orbital are shown in Figure 4. Major features are two peaks at 458.5 and 464.1 eV, which can be assigned to the spin-orbital split of Ti$_{2p}$ orbital. The Ti$_{2p 1/2}$ and Ti$_{2p 3/2}$ split is 5.6 eV and the intensity ratio is about 2:1. These are in agreement with previous reports on TiO$_2$. However, photoelectron emissions from Ti$^{4+}$ ions appear at binding energies 1.4 eV lower than their Ti$^{3+}$ counterparts. The appearance of reduced Ti ions implies the existence of oxygen vacancies. It is also observable that the intensity of Ti$^{3+}$ components increases with increasing deposition temperature and decreasing oxygen pressure during TiO$_2$ deposition. Therefore, the oxygen vacancy concentration increases accordingly. As summarized in Figure 5, the Ti$^{3+}$ components increase from 6.5% to 8.8% in TiO$_2$ deposited in 2.0 Pa oxygen when deposition temperature increases from 30 to 150°C. For TiO$_2$ deposited at 80°C, the Ti$^{3+}$ percentage is 1.8 times greater in samples deposited in background vacuum than those deposited in 2.0 Pa oxygen.

**Figure 5:** The percentage of Ti$^{3+}$ components as functions of TiO$_2$ deposition parameters.

4. Conclusions

In summary, resistive switching characteristics of Pt/TiO$_2$/PZT/LSMO heterostructures have been studied. An evolution from an interface controlled ferroelectric diode behavior to a bulk-controlled conductive filament behavior has been observed by modulating the oxygen vacancy concentration in the TiO$_x$ layer, which increases with increasing deposition temperature and decreasing oxygen pressure. In heterostructures with less oxygen vacancies, the PZT layers are highly resistive and the electrical transport is limited by electron injection from the interface Schottky barrier, which can be controlled by polarization switching in PZT. However, in heterostructures with more oxygen vacancies, the diffusion of oxygen vacancies into PZT results in a resistive switching behavior controlled by the formation and rupture of conductive filaments composed of conglomerated oxygen vacancies. These observations suggest that the resistive switching characteristics of bilayer heterostructures could be tuned by deposition parameters.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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**References**


[6] G.-S. Park, Y. B. Kim, S. Y. Park et al., ”In situ observation of filamentary conducting channels in an asymmetric Ta$_{2}$O$_{5–x}$/TaO$_{2–x}$ bilayer structure,” *Nature Communications*, vol. 4, article 2382, 2013.


