Research Article

Resistive Switching Characteristics in $\text{TiO}_2/\text{LaAlO}_3$ Heterostructures Sandwiched in Pt Electrodes

Yuyuan Cao, Qitao Di, Lin Zhu, Aidong Li, and Di Wu

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

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

Received 24 February 2015; Accepted 24 March 2015

Academic Editor: Yong Ding

Copyright © 2015 Yuyuan Cao et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

$\text{TiO}_2/\text{LaAlO}_3$ (TiO_2/LAO) heterostructures have been deposited on $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates by pulsed laser deposition. Resistive switching characteristics of $\text{Pt}/\text{TiO}_2/\text{LAO}/\text{Pt}$ have been studied and discussed in comparison with those of $\text{Pt}/\text{TiO}_2/\text{Pt}$. It is observed that the switching uniformity and the ON/OFF resistance ratio can be greatly improved by introducing the LAO layer. The observed resistive switching characteristics are discussed as a function of LAO thickness and explained by the preferential formation and rupture of conductive filaments, composed of oxygen vacancies, in the LAO layer.

1. Introduction

Resistive random access memories (RRAMs), in which binary logical states are represented by a low resistance and a high resistance state [1], have attracted considerable attention, due to their distinctive features and advantages meeting the demands of next generation high-speed [2, 3], low-power consumption [3], and high-density [4] memory devices. A variety of oxides, including binary metal oxides [5–8], perovskite dielectrics [9–12], and complex electron correlated oxides [13–16], have been demonstrated to show resistance switching behaviors, among which TiO_2 [17, 18] is one of the most extensively studied, owing to its unique advantages such as wide band gap, high temperature stability, and high dielectric constant with flexibility to exhibit both unipolar and bipolar switching characteristics. However, several issues, including device stability, endurance, and the ON/OFF resistance ratio [17], still need to be improved. Although a large ON/OFF resistance ratio about 10^4 has been reported in $\text{Pt}/\text{TiO}_2/\text{Pt}$ devices [19], most unipolar TiO_2 devices show an ON/OFF resistance ratio about 10~100, as in the $\text{Pt}/\text{TiO}_2/\text{TiN}$ devices reported by Choi and colleagues [20]. Some methods have been investigated to improve the resistance switching performance, such as doping impurities

[21, 22], optimizing electrode materials [23], and controlling the oxygen content of films [24].

Various models have been proposed to explain the resistive switching phenomenon. Liu et al. reported that the resistive switching performances of Zr^{+} -implanted- ZrO_2 films can be explained by charge trapping and detrapping [25]. Electrochemical migration of oxygen vacancies may result in resistive switching in $\text{TiO}_{2-\delta}/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ stacks [26]. Modification of Schottky barriers with interface states in Pt/Nb -doped SrTiO_3 Schottky junction [27] represents another important resistive switching mechanism. Specifically, the conductive filament model [28] has been widely accepted to explain the resistive switching behavior in binary oxides. In this model, resistive switching is achieved by formation and rupture of conductive filaments, which have been observed by *in situ* transmission electron microscopy [29, 30] and local conductivity measurement, due to the migration of charged species on the nanoscale [31].

In this paper, we report the improvement of resistive switching properties in $\text{Pt}/\text{TiO}_2/\text{Pt}$ heterostructures by inserting a LaAlO_3 (LAO) layer between TiO_2 and Pt bottom electrode. By comparing switching characteristics as a function of LAO thickness, it is proposed that the switching uniformity and ON/OFF resistance ratio can be improved by

the formation and rupture of conductive filaments in the LAO layer.

2. Experimental Section

TiO₂ thin films and TiO₂/LAO bilayers were deposited on Pt/TiO₂/SiO₂/Si substrates by pulsed laser deposition using a coherent CompexPro 205F KrF excimer laser with a 248 nm output at a repetition rate of 2 Hz. The oxygen pressure and substrate temperature during the deposition were maintained at 0.2 Pa and 350°C for TiO₂ and 0.1 Pa and 750°C for LAO, respectively. The thickness of TiO₂ was about 50 nm, while that of LAO varied from 10 to 30 nm. Pt top electrodes, 100 μ m in diameter, were sputter-deposited at room temperature, using a shadow mask. The surface morphology, chemical composition, and cross-sections of the heterostructures were characterized by an Asylum Research Cypher-ES atomic force microscopy (AFM), a Zeiss ULTRA 55 field emission scanning electron microscope (SEM), and a Thermo Fisher K-Alpha X-ray photoelectron spectroscope (XPS), respectively. The resistive switching behavior was measured using a Keithley 2400 source-measure unit. The bias voltage was applied on the top electrodes while the bottom electrode was always grounded.

3. Results and Discussion

Figure 1(a) shows the surface morphology of TiO₂/LAO deposited on Pt/TiO₂/SiO₂/Si substrates. A smooth surface with a root mean square roughness of about 1.3 nm is obtained over an area of $3 \times 3 \mu\text{m}^2$. Both TiO₂ and LAO layers are deposited below their crystallization temperature [32, 33] and are amorphous as indicated by X-ray diffraction. Figure 1(b) shows the cross-sectional SEM image of a TiO₂/LAO sample in which the LAO layer is deposited for 20 min. The total thickness of the TiO₂/LAO bilayer is about 80 nm. The deposition rate of LAO is calibrated separately as about 1.5 nm/min. Therefore, the thickness of TiO₂ and LAO in this sample is about 50 and 30 nm, respectively. We keep the thickness of TiO₂ at 50 nm throughout this paper. Figure 1(c) displays the XPS spectra of the Ti 2p core-level electron in TiO₂/LAO. The Ti 2p peak can be decomposed into four components, centered at 457.0, 458.3, 463.1, and 464.0 eV. Two strong peaks correspond to the spin-orbit split of Ti⁴⁺ 2p electrons [34, 35]. The other two peaks can be attributed to Ti³⁺ ions. As estimated from the integrated intensity of Ti⁴⁺ and Ti³⁺ components, there are about 4.5% Ti³⁺, indicating the existence of oxygen vacancies in TiO₂ [35].

Figure 2(a) shows 50 consecutive I-V curves of Pt/TiO₂/Pt devices in a semilogarithmic plot. The devices are initially in the low resistance state. A typical unipolar resistive switching can be observed. However, the critical voltages, at which the resistance toggles between a high and a low level, are quite dispersive. The reset voltage, at which the devices are switched from a low resistance state to a high resistance state, is from 1.3 to 1.7 V, while a voltage between 2.0 and 2.7 V can set the devices into the low resistance state.

TABLE 1: Switching voltages of Pt/TiO₂/Pt and Pt/TiO₂/LAO/Pt devices.

Sample	Average		Standard deviation	
	V_{set} (V)	V_{reset} (V)	V_{set} (V)	V_{reset} (V)
Pt/TiO ₂ /Pt	2.45	1.50	0.21	0.11
Pt/TiO ₂ /LAO/Pt	4.72	1.06	0.01	0.01

We then insert a layer of LAO, 30 nm in thickness, between TiO₂ and the bottom electrode. Figure 2(b) shows 50 consecutive I-V cycles of Pt/TiO₂/LAO/Pt devices. Contrary to the Pt/TiO₂/Pt devices, these devices are initially in the high resistance state. A +8.0 V electroforming voltage with 1 mA current compliance was applied and the resistive switching was triggered at +7.0 V. After the forming process, TiO₂/LAO bilayers sandwiched in Pt electrodes exhibit reproducible and uniform unipolar resistive switching characteristics. By sweeping the voltage from zero to about 1.0 V, the current drops abruptly and the devices are switched to the high resistance state. While sweeping the voltage again, a sudden jump of current appears at about 4.7 V, and the devices are set again into the low resistance state. A 10 mA current compliance was applied in the set process. The statistics of the set and reset voltages from 50 switching cycles are shown in Table 1. For the Pt/TiO₂/Pt devices, the standard deviations of set and reset voltages are 0.21 V and 0.11 V, respectively. However, after inserting the LAO layer, the standard deviations of set and reset voltages for Pt/TiO₂/LAO/Pt devices decrease to about 0.01 V. Although the Pt/TiO₂/Pt devices exhibit an ON/OFF resistance ratio about only 10^2 , the Pt/TiO₂/LAO/Pt devices could maintain a greatly improved ON/OFF ratio about 10^3 after 400 times consecutive switching, as shown in Figure 3.

In previous studies, the resistive switching behavior in TiO₂ has been reported to be governed by the formation and rupture of conducting filaments, which are formed by percolation of certain kind of charged defects such as oxygen vacancies [28]. Due to the random nature of filaments, uniform switching parameters are difficult to achieve. To improve the switching uniformity, Hirose et al. doped Co into TiO₂ thin films [22] and found that the conductive filaments preferentially formed or ruptured in the vicinity of the impurities. Chang et al. [36] embedded Pt nanocrystals into TiO₂ thin films sandwiched in Pt electrodes and improved the resistive switching uniformity by local enhancement of electric field adjacent to the Pt nanocrystals. Liu et al. [37] reported that compared with the TiN/TiO₂/Pt devices, by inserting a ZnO layer between the TiO₂ and Pt bottom electrode, the uniformity can be greatly improved because the distribution and migration of oxygen vacancies across the multilayers can be adjusted by the embedded ZnO layer. This can be used to explain the role that LAO plays in the improvement of resistive switching uniformity. In Pt/TiO₂/LAO/Pt devices, the resistivity of LAO is much higher than that of TiO₂ due to the wide band gap of LAO (about 5.5 eV). The high resistance LAO layer connected in series with semiconductive TiO₂ leads to the initial high resistance state in the Pt/TiO₂/LAO/Pt devices. However,

FIGURE 1: (a) Surface morphology, (b) cross-sectional SEM image, and (c) XPS spectra of the Ti 2p core-level electrons.

FIGURE 2: Typical resistive switching characteristics of (a) Pt/TiO₂/Pt and (b) Pt/TiO₂/LAO/Pt.

FIGURE 3: The reversible resistance switching behavior and ON/OFF resistance ratio for (a) Pt/TiO₂/Pt and (b) Pt/TiO₂/LAO/Pt. The read voltage is set at 0.1 V. The set and reset voltage are 5.0 and 2.0 V.

FIGURE 4: (a) Typical I-V curves of Pt/TiO₂/LAO/Pt devices and (b) ON and OFF state resistance of Pt/TiO₂/LAO/Pt devices as function of LAO thickness.

positive charged oxygen vacancies in TiO₂, as evidenced by the XPS results shown in Figure 1(c), can be driven into the LAO layer to form the conductive paths during the electro-forming process. The observation that both Pt/TiO₂/Pt and Pt/TiO₂/LAO/Pt devices exhibit identical resistance values in the low resistance state supports that conductive filaments are formed in LAO. In the high resistance state, the resistance in Pt/TiO₂/LAO/Pt is two orders higher than that of Pt/TiO₂/Pt. This indicates the preferential rupture of the conductive filaments in LAO, which sets the LAO layer back into insulator. This also makes the ON/OFF resistance ratio of Pt/TiO₂/LAO/Pt 10 times greater than that of Pt/TiO₂/Pt devices.

To check the scenario proposed, resistive switching characteristics of Pt/TiO₂/LAO/Pt devices with various LAO

thicknesses are compared, as shown in Figure 4(a). The resistance of the ON and the OFF states is summarized in Figure 4(b). With increasing the thickness of LAO layer, all the devices show approximately the same resistance values in low resistance ON state, while the resistance value in high resistance OFF state increases. The set voltage shows a strong dependence on the thickness of LAO layer, increasing from 2.2 to 4.7 V with the increase of LAO thickness from 0 to 30 nm. This can be ascribed to the increase of LAO resistance. However, the reset voltage decreases from 1.4 to 1.0 V by inserting the LAO layer and does not change with the thickness of LAO. This indicates that the LAO layer is conductive in the low resistance state. These observations further confirm that the conductive filament is formed and ruptured preferentially in LAO layer.

4. Conclusions

By introducing a LAO layer into TiO_2 and the Pt bottom electrode, we improved the resistive switching characteristics in TiO_2 based heterostructures. The dispersion of switching voltage in $\text{Pt/TiO}_2/\text{Pt}$ is greatly suppressed and the ON/OFF resistance ratio has been increased from 10^2 to 10^3 by inserting a LAO layer of 30 nm in thickness. XPS measurements reveal an amount of oxygen vacancies in the TiO_2 layer. These oxygen vacancies may be driven into the LAO layer, which shows an initial high resistance. The resistance of the high resistance state increases with the LAO thickness, while that of the low resistance state is insensitive of the LAO thickness. These indicate the preferential formation and rupture of conductive filaments in the LAO layer.

Conflict of Interests

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

Acknowledgments

This work was jointly sponsored by the State Key Program for Basic Research of China (2015CB921203), the Natural Science Foundation of China (51222206 and 11374139), and the Jiangsu Provincial Natural Science Foundation (BK2012016).

References

- [1] G. Dearnaley, A. M. Stoneham, and D. V. Morgan, "Electrical phenomena in amorphous oxide films," *Reports on Progress in Physics*, vol. 33, no. 3, pp. 1129–1191, 1970.
- [2] M. J. Rozenberg, I. H. Inoue, and M. J. Sánchez, "Nonvolatile memory with multilevel switching: a basic model," *Physical Review Letters*, vol. 92, no. 17, Article ID 178302, 2004.
- [3] M.-C. Wu, W.-Y. Jang, C.-H. Lin, and T.-Y. Tseng, "A study on low-power, nanosecond operation and multilevel bipolar resistance switching in $\text{Ti/ZrO}_2/\text{Pt}$ nonvolatile memory with 1T1R architecture," *Semiconductor Science and Technology*, vol. 27, no. 6, Article ID 065010, 2012.
- [4] K. P. Biju, X. Liu, J. Shin et al., "Highly asymmetric bipolar resistive switching in solution-processed $\text{Pt/TiO}_2/\text{W}$ devices for cross-point application," *Current Applied Physics*, vol. 11, no. 4, supplement, pp. S102–S106, 2011.
- [5] L. Goux, J. G. Lisoni, M. Jurczak, D. J. Wouters, L. Courtade, and C. Muller, "Coexistence of the bipolar and unipolar resistive-switching modes in NiO cells made by thermal oxidation of Ni layers," *Journal of Applied Physics*, vol. 107, no. 2, Article ID 024512, 2010.
- [6] S.-Y. Wang, C.-H. Tsai, D.-Y. Lee, C.-Y. Lin, C.-C. Lin, and T.-Y. Tseng, "Improved resistive switching properties of $\text{Ti/ZrO}_2/\text{Pt}$ memory devices for RRAM application," *Microelectronic Engineering*, vol. 88, no. 7, pp. 1628–1632, 2011.
- [7] A. Prakash, S. Maikap, C. S. Lai et al., "Bipolar resistive switching memory using bilayer TaO_x/WO_x films," *Solid-State Electronics*, vol. 77, pp. 35–40, 2012.
- [8] B. J. Choi, D. S. Jeong, S. K. Kim et al., "Resistive switching mechanism of TiO_2 thin films grown by atomic-layer deposition," *Journal of Applied Physics*, vol. 98, no. 3, Article ID 033715, 2005.
- [9] D. X. Chen, A. D. Li, and D. Wu, "Resistive switching in BiFeO_3 -based heterostructures due to ferroelectric modulation on interface Schottky barriers," *Journal of Materials Science: Materials in Electronics*, vol. 25, pp. 3251–3256, 2014.
- [10] K. Li, Z. Wen, D. Wu, H. F. Zhai, and A. D. Li, "Bipolar resistive switching based on $\text{SrTiO}_3/\text{YBa}_2\text{Cu}_3\text{O}_7$ epi-layers," *Journal of Physics D: Applied Physics*, vol. 46, no. 3, Article ID 035308, 2013.
- [11] J.-Y. Lin and C.-L. Wu, "Bipolar switching characteristics of RRAM cells with $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ film," *Advances in Materials Science and Engineering*, vol. 2014, Article ID 425085, 7 pages, 2014.
- [12] J. Wu, Z. Wen, D. Wu, H. Zhai, and A. Li, "Current-voltage characteristics of sol-gel derived SrZrO_3 thin films for resistive memory applications," *Journal of Alloys and Compounds*, vol. 509, no. 5, pp. 2050–2053, 2011.
- [13] V. Dubost, T. Cren, C. Vaju et al., "Resistive switching at the nanoscale in the Mott insulator compound GaTa_4Se_8 ," *Nano Letters*, vol. 13, no. 8, pp. 3648–3653, 2013.
- [14] J. Sakai and M. Kurisu, "Effect of pressure on the electric-field-induced resistance switching of VO_2 planar-type junctions," *Physical Review B*, vol. 78, Article ID 033106, 2008.
- [15] R. Yang and X. M. Li, "Improvement of resistance switching properties for metal/ $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{Pt}$ devices," *Physica Status Solidi (A)*, vol. 208, no. 5, pp. 1041–1046, 2011.
- [16] Q. Wang, D. S. Shang, Z. H. Wu, D. Chen, and X. M. Li, "'Positive' and 'negative' electric-pulse-induced reversible resistance switching effect in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films," *Applied Physics A*, vol. 86, no. 3, pp. 357–360, 2007.
- [17] D. Acharyya, A. Hazra, and P. Bhattacharyya, "A journey towards reliability improvement of TiO_2 based resistive random access memory: a review," *Microelectronics Reliability*, vol. 54, no. 3, pp. 541–560, 2014.
- [18] S. K. Kim, K. M. Kim, D. S. Jeong, W. Jeon, K. J. Yoon, and C. S. Hwang, "Titanium dioxide thin films for next-generation memory devices," *Journal of Materials Research*, vol. 28, no. 3, pp. 313–325, 2013.
- [19] K. M. Kim, B. J. Choi, D. S. Jeong, and C. S. Hwang, "Influence of carrier injection on resistive switching of TiO_2 thin films with Pt electrodes," *Applied Physics Letters*, vol. 89, no. 16, Article ID 162912, 2006.
- [20] B. J. Choi, S. Choi, K. M. Kim et al., "Study on the resistive switching time of TiO_2 thin films," *Applied Physics Letters*, vol. 89, no. 1, Article ID 012906, 2006.
- [21] D. Mardare and G. I. Rusu, "Comparison of the dielectric properties for doped and undoped TiO_2 thin films," *Journal of Optoelectronics and Advanced Materials*, vol. 6, no. 1, pp. 333–336, 2004.
- [22] S. Hirose, A. Nakayama, H. Niimi, K. Kageyama, and H. Takagi, "Improvement in resistance switching and retention properties of Pt/TiO_2 Schottky junction devices," *Journal of the Electrochemical Society*, vol. 158, no. 3, pp. H261–H266, 2011.
- [23] S. C. Oh, H. Y. Jung, and H. Lee, "Effect of the top electrode materials on the resistive switching characteristics of TiO_2 thin film," *Journal of Applied Physics*, vol. 109, no. 12, Article ID 124511, 2011.
- [24] Y. Li, Y. Wang, S. Liu et al., "Improvement of resistive switching uniformity in TiO_x film by nitrogen annealing," *Journal of the Korean Physical Society*, vol. 58, no. 3, pp. L407–L410, 2011.

- [25] Q. Liu, W. H. Guan, S. B. Long, R. Jia, M. Liu, and J. N. Chen, "Resistive switching memory effect of ZrO_2 films with Zr^{+} implanted," *Applied Physics Letters*, vol. 92, no. 1, Article ID 012117, 2008.
- [26] Y. S. Chen, B. Chen, B. Gao et al., "Understanding the intermediate initial state in $\text{TiO}_{2-\delta}/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ stack-based bipolar resistive switching devices," *Applied Physics Letters*, vol. 99, no. 7, Article ID 072113, 2011.
- [27] H. Sim, D.-J. Seong, M. Chang, and H. Hwang, "Excellent resistance switching characteristics of Pt/single-crystal Nb-doped SrTiO_3 Schottky junction," in *Proceedings of the 21st IEEE Non-Volatile Semiconductor Memory Workshop (NVSMW '06)*, pp. 88–89, Monterey, Calif, USA, February 2006.
- [28] K. M. Kim, D. S. Jeong, and C. S. Hwang, "Nanofilamentary resistive switching in binary oxide system; a review on the present status and outlook," *Nanotechnology*, vol. 22, no. 25, Article ID 254002, 2011.
- [29] Z. Xu, Y. Bando, W. L. Wang, X. D. Bai, and D. Golberg, "Real-time in situ HRTEM-resolved resistance switching of Ag_2S nanoscale ionic conductor," *ACS Nano*, vol. 4, no. 5, pp. 2515–2522, 2010.
- [30] D.-H. Kwon, K. M. Kim, J. H. Jang et al., "Atomic structure of conducting nanofilaments in TiO_2 resistive switching memory," *Nature Nanotechnology*, vol. 5, no. 2, pp. 148–153, 2010.
- [31] S. C. Chae, J. S. Lee, S. Kim et al., "Random circuit breaker network model for unipolar resistance switching," *Advanced Materials*, vol. 20, no. 12, pp. 1154–1159, 2008.
- [32] W.-G. Kim and S.-W. Rhee, "Effect of post annealing on the resistive switching of TiO_2 thin film," *Microelectronic Engineering*, vol. 86, no. 11, pp. 2153–2156, 2009.
- [33] K.-C. Liu, W.-H. Tzeng, K.-M. Chang et al., "Investigation of the effect of different oxygen partial pressure to LaAlO_3 thin film properties and resistive switching characteristics," *Thin Solid Films*, vol. 520, no. 4, pp. 1246–1250, 2011.
- [34] Y. D. Zhu, M. Y. Li, H. Zhou et al., "Nonvolatile bipolar resistive switching in an $\text{Ag}/\text{TiO}_2/\text{Nb}:\text{SrTiO}_3/\text{In}$ device," *Journal of Physics D: Applied Physics*, vol. 45, Article ID 375303, 2012.
- [35] J. Zhang, Q. T. Li, S. Q. Li et al., "An efficient photoanode consisting of TiO_2 nanoparticle-filled TiO_2 nanotube arrays for dye sensitized solar cells," *Journal of Power Sources*, vol. 268, pp. 941–949, 2014.
- [36] W.-Y. Chang, K.-J. Cheng, J.-M. Tsai et al., "Improvement of resistive switching characteristics in TiO_2 thin films with embedded Pt nanocrystals," *Applied Physics Letters*, vol. 95, no. 4, Article ID 042104, 2009.
- [37] L. Liu, D. Yu, B. Chen et al., "Improvement of reliability characteristics of TiO_2 -based resistive switching memory device with an inserted ZnO layer," *Japanese Journal of Applied Physics*, vol. 51, no. 10, Article ID 101101, 2012.