Resistive Switching Characteristics of TiO_2 Films with Embedded Co Ultra Thin Layer

Young Ho Do, June Sik Kwak, and Jin Pyo Hong

Abstract—**We systematically investigated the resistive switching properties of thin TiO_2 films on Pt/Ti/SiO_2/Si substrates that were embedded with a Co ultra thin layer. An in-situ sputtering technique was used to grow both films without breaking the chamber vacuum. A stable bipolar switching in the current-voltage curve was clearly observed in TiO_2 films with an embedded Co ultra thin layer, addressing the high and low resistive state under a bias voltage sweep. We propose that the underlying origin involved in the bipolar switching may be attributed to the interface redox reaction between the Co and TiO_2 layers. The improved reproducible switching properties of our novel structures under forward and reverse bias stresses demonstrated the possibility of future non-volatile memory elements in a simple capacitive-like structure.**

Index Terms—**ReRAM, nonvolatile memory, bipolar switching, TiO_2 films with embedded Co ultra thin layer**

I. INTRODUCTION

Several new types of nonvolatile memories (NVMs), such as a phase change memory, magnetoresistive memory, nanofloating gate memory (NFGM), and ferroelectric memory, have been extensively studied because their conventional NVM properties are approaching their scaling limits [1-4]. Resistive random access memory (ReRAM) is another interesting competitor in the NVM class. The ReRAM device has been even more extensively evaluated because of its simple structure, long retention time, small size, fast switching speed, and nondestructive readout [5-8]. This resistive switching effect may not only open a new area of research in fundamental physics, but may also provide a variety of possible applications. However, the resistive switching origin of various oxide materials is still unclear, although the switching behaviors have been clearly observed and some theoretical models have already been suggested, such as the Schottky barriers model [9], the filamentary model [10], the space charge limited current model [11] and the Mott transition model [6].

The ReRAM was recently studied using two types of oxide materials, binary oxide materials (unipolar switching) [12-16] and perovskite materials (bipolar switching) [17-21]. The polarities of the external voltage for the reset and set processes are identical in unipolar switching, while they are opposite in bipolar switching. However, unipolar switching has faults in terms of a high operating current, compliance current, and its forming process. Therefore, bipolar switching may have better merits than unipolar switching in terms of better uniformity, faster switching speed, and non-compliance current.

We report on the switching properties of TiO_2 films with an embedded Co ultra thin layer in this paper using mainly the electrical measurements. The structural properties of TiO_2 films were characterized using X-ray diffraction (XRD) and a scanning electron microscope (SEM). In addition, the bipolar switching behavior of TiO_2 films with an embedded Co layer was clearly observed when the resistance was changed by two orders of magnitude. These experimental results might provide useful information for better understanding the origin of

---

Manuscript received Feb. 27, 2008; revised Mar. 10, 2008.

New functional materials and devices lab, Department of Physics, Hanyang University, Seoul 133-791, Korea
Tel.: +82-2-2220-0911; fax: +82-2-2296-3738.
E-mail : jphong@hanyang.ac.kr

the I-V hysteresis loop and the principle of resistive switching in our oxide materials.

II. EXPERIMENTS

Polycrystalline TiO_2 films were grown on $Pt/Ti/SiO_2/Si$ substrates by using a reactive rf sputtering technique. The deposition rate information for various working pressures and the O_2 flow rate are given elsewhere [22]. An ultra thin Co layer was *in-situ* prepared using a layer-by-layer growth method with a dc sputtering system after the deposition of the bottom TiO_2 layer, and then this growth was followed again by the deposition of TiO_2 film. The deposition was done at a base pressure of $7x10^{-8}$ Torr without any vacuum break. Finally, a Pt top electrode was deposited by a dc sputtering system using a lift-off photolithographic process. The thickness of the electrode layer was 100 nm, and the diameters of the electrodes were 200 μm. Fig. 1 shows the basic structure of a TiO_2 film with an embedded Co ultra thin layer ($Pt/TiO_2/Co/TiO_2/Pt$).

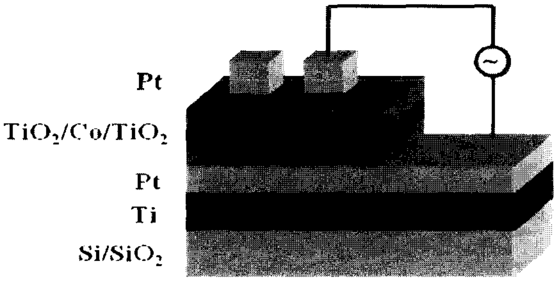


Fig. 1. Schematic structure of TiO_2 films with embedded Co ultra thin layer.

III. RESULTS AND DISCUSSIONS

The crystalline structure of TiO_2 films with an embedded Co layer grown on Si (100) substrates were analyzed by XRD, as shown in Fig. 2. The XRD pattern clearly has a peak of *R*(110), implying a rutile phase in TiO_2 films. The embedded Co layer also exhibited a polycrystalline phase. In addition, we observed a slight shift in the position of the main peak, resulting from a residual strain between the TiO_2 films and the substrates.

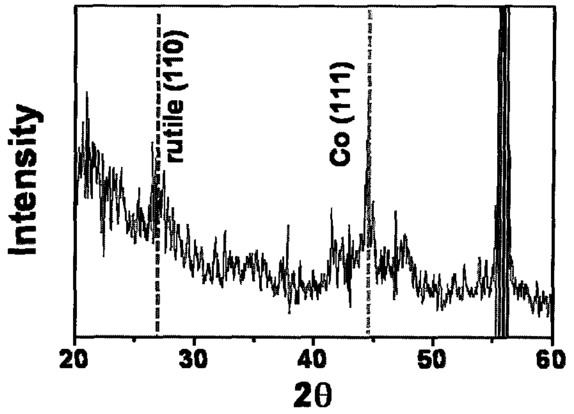


Fig. 2. X-ray diffraction pattern of TiO_2 films with embedded Co ultra thin layer.

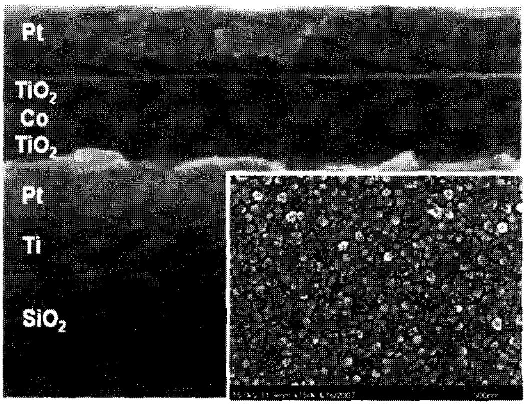


Fig. 3. Cross-sectional image from scanning electron microscope of TiO_2 films with embedded Co ultra thin layer. The inset is the surface image of TiO_2 films with embedded Co ultra thin layer.

The cross-sectional and surface SEM images of TiO_2 films with an embedded Co layer that were deposited on Pt bottom electrodes are shown in Fig. 3. The cross-sectional SEM image exhibit a good interface between the TiO_2 and Co layers, which plays an important role in the resistive switching behavior (Fig. 3 (b)) [6, 21, 23]. As shown in the inset of Fig. 3, the TiO_2 film with an embedded Co layer consists of fine grains.

Fig. 4 shows the I-V characteristics of TiO_2 films with an embedded Co layer, indicating the bipolar switching behaviors. As can be seen, the I-V curves show that a sudden increase in current occurred near the 4.3 V under current limitation at 10 mA. This is called the forming process. After the forming process, the sample starts in the LRS when the voltage is swept from zero to positive values. In the subsequent voltage sweeping from positive to negative voltage, the sample shows an increased resistance, which is called the Reset-process. At a

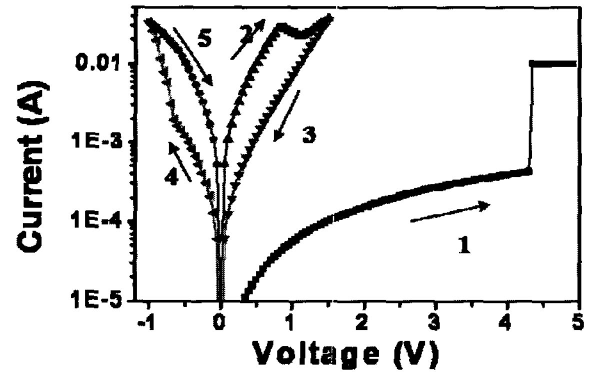


Fig. 4. Typical resistive switching I-V curves of TiO_2 films with embedded Co ultra thin layer.

negative voltage the sample resistance switches back from HRS to LRS, which is the so-called Set-process. The I-V curves are slightly asymmetric between the positive and negative sides. It is expected that the reproducible resistive change is related to the oxygen vacancy movement under electrical field switching in the forming process. This behavior is common in binary oxide materials that typically indicate unipolar switching [9, 24]. Thereafter, the bipolar switching may take place due to the redox reaction between the TiO_2 films and the Co layer; that is, according to the applied electric field polarity, the bipolar switching behavior in TiO_2 films with an embedded Co layer is relevant to the interface effect between the Co and TiO_2 layers by the oxygen ions. According to our proposal, we assume that oxygen defects and oxygen vacancies in TiO_2 films with embedded Co layer co-exist, and correspond to a great influence of these defects on their resistive switching properties.

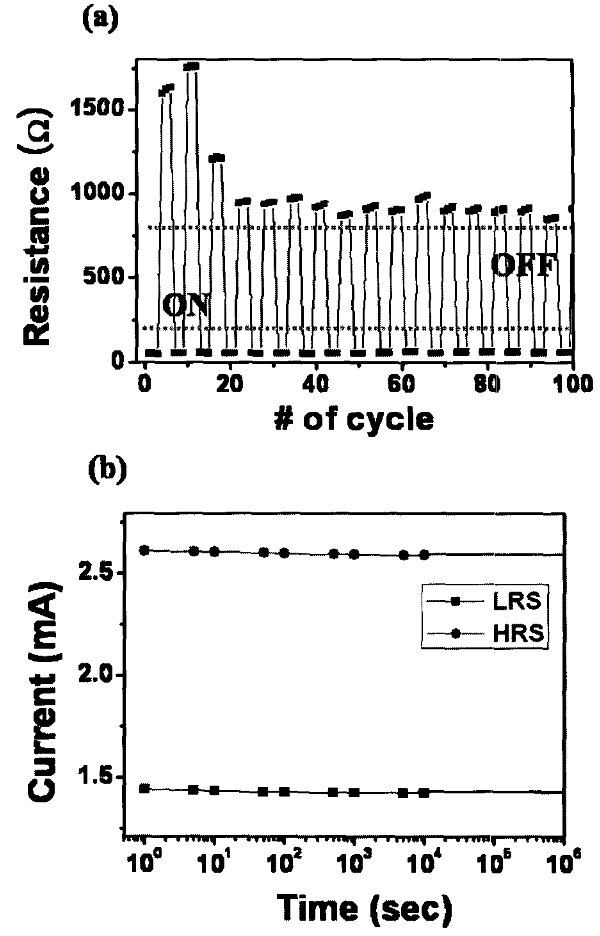


Fig. 5. Graphs of results of (a) endurance and (b) retention test of b) TiO_2 films with embedded Co ultra thin layer. (read voltage : 0.2 V)

Fig. 5 (a) shows the resistance of the HRS and LRS versus the number of switching cycles of the TiO_2 films with an embedded Co layer at a reading voltage of 0.2 V. As we can see from this figure, the switching behaviors of our films had 10 resistance ratios and the on-off resistance state gradually stabilized with respect to the number of cycles; this was sufficiently large for the periphery circuits to probe the different resistance states. Moreover, our films have a set operational voltage (set-voltage: -1.2 V, reset-voltage: +1.5 V). The retention characteristics of the devices measured at RT are shown in Fig. 5 (b). The readout voltage was 0.2 V. Fig. 5 (b) shows the current variation over time for both the HRS and the LRS of TiO_2 films with an embedded Co layer. As can be seen, the HRS and LRS states were retained for 10^4 s without using an external bias voltage, and there is no remarkable degradation, confirming the possible nonvolatile application of the device. We expect that the long data retention results obtained for our material may help to eliminate the possible effects of using interface charge trapping as a switching mechanism, as expected by another group [11].

We believe that there is a good possibility of making TiO_2 films with an embedded Co layer more suitable for future ReRAM applications by modifying the device fabrication parameters in order to improve the ratio of the ON/OFF state resistance, the write-read-erase-read cycle number, and the switching speed of future works. More work is currently being done on structural variations.

IV. CONCLUSIONS

We observed bipolar resistive switching in TiO_2 films with an embedded Co ultra-thin layer that does not occur in typical binary oxide materials. The magnitude and polarity of bipolar switching behaviors depend on the Co insertion layer in TiO_2 films. We propose that the bipolar switching in our structure is related to the redox reaction between the TiO_2 films and the Co insertion layer. TiO_2 films with an embedded Co ultra thin layer could give rise to the promise of future non-volatile memory applications if superior memory characteristics, such as long retention time, simple structure, and good uniformity, are considered.

ACKNOWLEDGMENTS

This project was supported by "The National Research Program for 0.1-Terabit Non-volatile Memory Development" sponsored by the Korea Ministry of Commerce, Industry and Energy.

REFERENCES

[1] S. Lai, T. Lowrey, *Int. Electron Devices Meet. Tech. Dig.* (2001) 803.

[2] G. A. Prinz, *Science* 282 (1998) 1660.

[3] T. Hayashi, Y. Igarashi, D. Inomata, T. Ichimori, T. Mitsuhashi, K. Ashikaga, T. Ito, M. Yoshimaru, M. Nagata, S. Mitarai, H. Godaiin, T. Nagahama, C. Isobe, H. Moriya, M. Shoji, Y. Ito, H. Kuroda, and M. Sasaki, *Int. Electron Devices Meet. Tech. Dig.* (2002) 543.

[4] A. Chen, S. Haddad, Y. C. Wu, T. N. Fang, Z. Lan, S. Avanzino, S. Pangrle, M. Buynoski, M. Rathor, W. Cai, N. Tripsas, C. Bill, M. VanBuskirk, and M. Taguchi, *Int. Electron Devices Meet. Tech. Dig.* (2005) 746.

[5] Y. Watanabe, J. G. Bednorz, A. Bietsch, Ch. Gerber, D. Widmer, A. Beck, and S. J. Wind, *Appl. Phys. Lett.* 78 (2001) 3738.

[6] M. J. Rozenberg, I. H. Inoue, and M. J. Sánchez, *Phys. Rev. Lett.* 92 (2004) 178302-1.

[7] I. G. Baek, D. C. Kim, M. J. Lee, H.-J. Kim, E. K. Yim, M. S. Lee, J. E. Lee, S. E. Ahn, S. Seo, J. H. Lee, J. C. Park, Y. K. Cha, S. O. Park, H. S. Kim, I. K. Yoo, U.-I. Chung, J. T. Moon, B. I. Ryu, *Int. Electron Devices Meet. Tech. Dig.* (2005) 750.

[8] H. Sim, H. Choi, D. Lee, M. Chang, D. Choi, Y. Son, E.-H. Lee, W. Kim, Y. Park, I.-K. Yoo, and H. Hwang, *Int. Electron Devices Meet. Tech. Dig.* (2005) 758.

[9] K. Szot, W. Speier, G. Bihlmayer, and R. Waser, *Nat. Mater.* 5 (2006) 312.

[10] S. Seo, M. J. Lee, D. C. Kim, S. E. Ahn, B.-H Park, Y. S. Kim, I. K. Yoo, I. S. Byun, I. R. Hwang, S. H. Kim, J.-S. Kim, J. S. Choi, J. H. Lee, S. H. Jeon, S. H. Hong, and B. H. Park, *Appl. Phys. Lett.* 87 (2005) 263507.

[11] T. N. Fang, S. Kaza, S. Haddad, A. Chen, Y. C. Wu, Z. Lan, S. Avanzino, D. Liao, C. Gopalan, S. Choi, S. Mahdavi, M. Buynoski, Y. Lin, C. Marrian, C. Bill, M. V. Buskirk, and M. Taguchi, *IEEE International Electron Devices Meeting 2006*, IEDM '06 Technical Digest. IEEE International, (2006) 1.

[12] T. W. Hickmott, *J. Appl. Phys.* 36 (1965) 1885.

[13] W. R. Hiatt, and T. W. Hickmott, *Appl. Phys. Lett.* 6 (1965) 106.

[14] K. L. Chopra, *J. Appl. Phys.* 36 (1965) 184.

[15] F. Argall, *Solid-State Electron.* 11 (1968) 535.

[16] T. W. Hickmott, *J. Vac. Sci. Technol.* 6 (1969) 828.

[17] A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, *Nature* (London) 388 (1997) 50.

[18] A. Beck, J. G. Bednorz, Ch. Gerber, C. Rossel, and D. Widmer, *Appl. Phys. Lett.* 77 (2000) 139.

[19] S. Q. Liu, N. J. Wu, and A. Ignatiev, *Appl. Phys. Lett.* 76 (2000) 2749.

[20] C. Rossel, G. I. Meijer, D. Bremaud, and D. Widmer, *J. Appl. Phys.* 90 (2001) 2892.

[21] S. Tsui, A. Baikalov, J. Cmaidalka, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, C. W. Chu, L. Chen, and A. J. Jacobson, *Appl. Phys. Lett.* 85 (2004) 317.

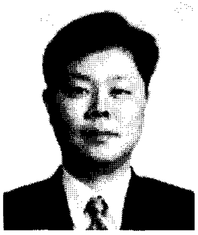
[22] Y. H. Do, K. W. Jeong, C. O. Kim, and J. P. Hong, *J. Korea Phys. Soc.* 48 (2006) 1492.

[23] A. Sawa, T. Fujii, M. Kawasaki, and Y. Tokura, *Appl. Phys. Lett.* 85 (2004) 4073.

[24] A. Baikalov, Y. Q. Wang, B. Shen, B. Lorenz, S. Tsui, Y. Y. Sun, and Y. Y. Xue, C. W. Chu, *Appl. Phys. Lett.*, 83 (2003) 957.

Young Ho Do received the B.S. degree in department of physics from Hanyang University, Korea, in 2002, and M.S. degree in department of physics from Hanyang University, Korea, in 2004. He is presently working towards his Ph.D. degree under supervision of Prof. J.P. Hong in Hanyang University, Korea. His current research interests are in the field of oxide materials, their characterization and application as nonvolatile memory and electronic devices.

June Sik Kwak received the B.S. degree in physics from Hoseo University, Chungnam, Korea, in 1997, and the M.S. degree in physics from Hanyang University, Seoul, Korea, in 2000. From 2004 to 2006, he was a Senior Researcher with the RFtron Inc., Seoul, Korea. He is currently working toward the Ph.D. degree at the Physics Department, Hanyang University. His research interests include transport property of metal oxide thin films and resistive switching effect of transition metal oxide for non-volatile memory application.



Jin Pyo Hong received his B.S. and Ph.D degrees in department of physics from University of California, Los Angeles (UCLA) in 1986 and 1992. From 1992 and 1998, He worked at Samsung Advanced institute of technology in Korea for six years up to 1988, where as a team leader, he served ad a team leader focusing on the development of new material and device and flat panel display, such as field emission display including metal and semiconductor microtips, phosphors, nano fabrication, and microwave device, etc. He joined the faculty of the department of physics in Hanyang univeristy as an assistant profess on 1998 and he is currently a professor at the same university. His main research area is to develop novel functional materials and devices, such as spin-related devices with spin MOS, spin wave, and TMR device, low dimensional structural material including nano wire, rod and various quantum dots for functionalized LED devices. Other key interest is to develop non-volatile memory devices including ReRAM and NFGM.