Endurance Improvement Technology With Nitrogen Implanted in the Interface of $WSiO_x$ Resistance Switching Device

Yong-En Syu, Rui Zhang, Ting-Chang Chang, *Senior Member, IEEE*, Tsung-Ming Tsai, Kuan-Chang Chang,
Jen-Chung Lou, Tai-Fa Young, Jung-Hui Chen, Min-Chen Chen, Ya-Liang Yang, Chih-Cheng Shih,
Tian-Jian Chu, Jian-Yu Chen, Chih-Hung Pan, Yu-Ting Su, Hui-Chun Huang,
Der-Shin Gan, and Simon M. Sze, *Life Fellow, IEEE*

***Abstract*—Incorporation of nitrogen as an oxygen-confining layer in the resistance switching reaction region is investigated to improve the reliability of resistance random access memory (RRAM). The switching mechanism can be attributed to the formation and rupture of conduction filaments. A compatible WSiON (around 5 nm) layer is introduced at the interface of tungsten silicon oxide ($WSiO_x$) and TiN electrode to prevent the randomly diffusing oxygen ions surpassing the storage region of the WSiON layer. The double-layer $WSiO_x$/WSiON memory structure would enhance the endurance over 100 times so as to better confirm the $WSiO_x$ RRAM application of nonvolatile memory.**

***Index Terms*—Nonvolatile memory, resistance switching, tungsten silicon oxide ($WSiO_x$).**

I. INTRODUCTION

RESISTANCE random access memory (RRAM) composed of an insulating layer sandwiched by two electrodes has recently attracted great attention as a candidate of next-generation nonvolatile memory applications [1]–[4]. In such metal–insulator–metal cells, the insulating layer (switching layer) exhibits reversible electric-field-induced resistance switching between the high-resistance state (HRS) and the low-resistance state (LRS). Heretofore, the resistance switching effect has been observed in various materials [5]–[9], and using different methods like $SCCO_2$ to modify the material characteristics also attracts lot of researchers to investigate [10], [11]. Among those materials, oxide materials are most widely investigated and the resistance switching is generally considered as a result of the formation and rupture of the localized conduction filament [12]–[14]. In this letter, the $WSiO_x$ film was taken as the resistive switching layer in Pt/$WSiO_x$/TiN memory cells. As it is quite easy for single-layer devices to get stressed from switching cycling and become irreversibly injured, a compatible WSiON layer is proposed to be inserted between $WSiO_x$ and TiN as an oxygen-confined layer to enhance memory switching parameters. It is a simple and efficient method to greatly enhance the resistance switching parameters that only need the introduction of ammonia in the manufacturing process.

II. EXPERIMENTAL SETUP

The patterned TiN/SiO_2/Si substrate was fabricated with standard deposition and etching process, after which via holes of different sizes can be formed (inset of Fig. 2). Then a 25-nm-thick $WSiO_x$ film was deposited into the via holes by RF magnetron sputter using a tungsten-silicide target at room temperature. Similarly, for improved memory devices, first 5-nm-thick WSiON layer was deposited by cosputtering SiO_2 and WSi_x targets in Ar/NH_3 = 30 sccm/10 sccm mixed gas ambient. And the sputtering power was fixed at RF power 200 and 20 W for SiO_2 and WSi_x targets respectively. After that 20 nm-thick $WSiO_x$ films were deposited with a gas ambient condition of Ar/O_2 = 30 sccm/10 sccm. Finally, the 80-nm-thick Pt film was capped to complete Pt/$WSiO_x$/TiN and Pt/$WSiO_x$/WSiON/TiN memory cells by DC magnetron sputtering. All the electric characteristics were measured by the Agilent B1500 semiconductor parameter analyzer. The DC sweeping and pulse bias were applied to the bottom electrode (TiN) while the top electrode (Pt) was grounded during the electrical measurements.

III. RESULTS AND DISCUSSION

Fig. 1 shows the comparison of typical bipolar resistance switching characteristics between Pt/$WSiO_x$/TiN and

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Y.-E. Syu, T.-C. Chang, M.-C. Chen, J.-Y. Chen, and Y.-T. Su are with the Department of Physics, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, and also with the Advanced Optoelectronics Technology Center, National Cheng Kung University, Tainan 70101, Taiwan (e-mail: tcchang@mail.phys.nsysu.edu.tw).

R. Zhang and J.-C. Lou are with the School of Software and Microelectronics, Peking University, Beijing 100871, China.

T.-M. Tsai, K.-C. Chang, T.-J. Chu, C.-H. Pan, H.-C. Huang, and D.-S. Gan are with the Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan.

T.-F. Young and Y.-L. Yang are with the Department of Mechanical and Electro-Mechanical Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan.

J.-H. Chen and C.-C. Shih is with the Department of Chemistry, National Kaohsiung Normal University, Kaohsiung 80201, Taiwan.

S. M. Sze is with the Department of Electronics Engineering, National Chiao Tung University, Hsinchu 300, Taiwan.

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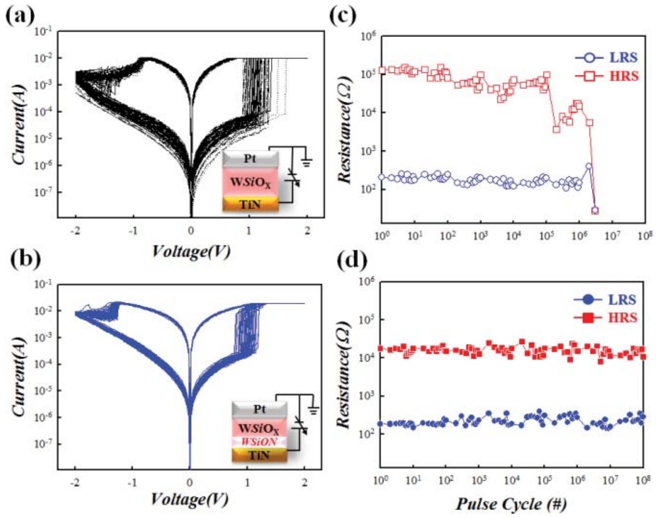

Fig. 1. Typical bipolar resistance switching I–V curves of the (a) Pt/WSiO$_X$/TiN and (b) Pt/WSiO$_X$/WSiON/TiN cells. (c) and (d) Corresponding endurance characteristics.

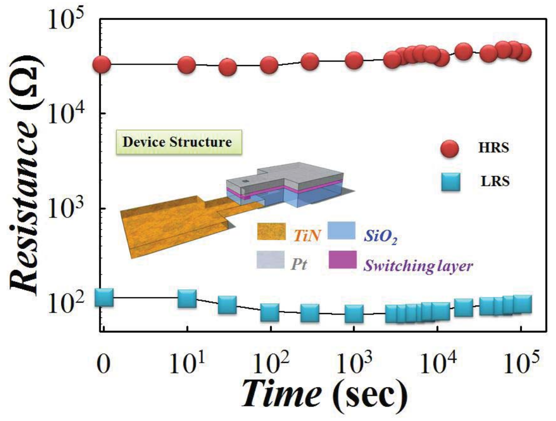

Fig. 2. Retention properties of double layer structure device at 85 °C. Inset: Device structure.

Pt/WSiO$_X$/WSiON/TiN devices. A compliance current of 10 mA was assigned to prevent permanent dielectric breakdown during the set process. From Fig. 1(a) and (b), it can be observed that single-layer RRAM devices exhibited unstable resistance switching properties, including resistance states and switching voltage. Fig. 1(c) and (d) shows the endurance of these two types of devices with respect to the switching cycles in AC voltage-pulse mode. The resistance values in HRS and LRS were extracted from the I–V curves at a read voltage of 0.1 V. The large variation of HRS for the single-layer RRAM indicates the memory cell is less reliable than the bilayer RRAM device whose endurance property is still satisfactory even after 10^8 cycles. In order to further confirm the performance of the double-layer device, retention was measured. It can be seen that both HRS and LRS remain stable after 10^5 s at 85 °C. (Fig. 2).

Fig. 3 reveals the stability properties of these two kinds of devices. Fig. 3(a) and (b) shows the distributions of switching voltage during the set process of monolayer and bilayer RRAMs, respectively. It is noted that bilayer devices have tighter distributions of set voltage. Furthermore, from the

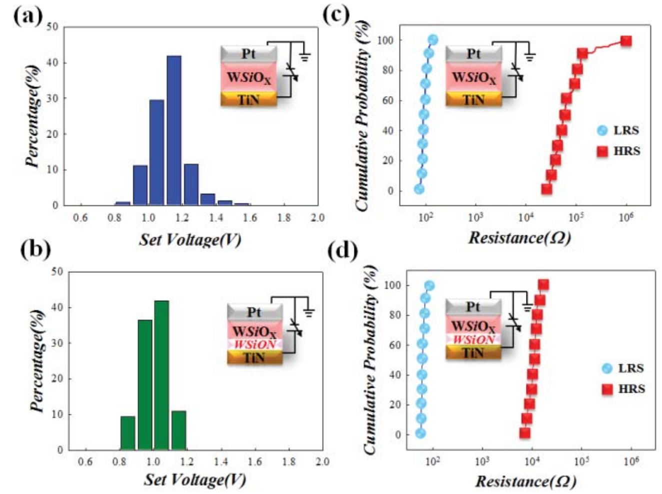

Fig. 3. Distributions of the (a) set voltage of monolayer and (b) bilayer RRAM devices. (c) and (d) Corresponding cumulative probability of HRS and LRS.

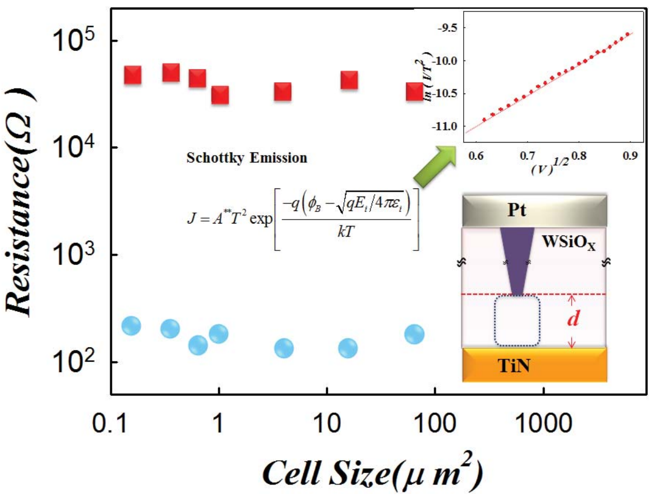

Fig. 4. Cell area independence of the resistance value in HRS and LRS. Inset: I–V curve fitting with Schottky emission mechanism and the switching range schematic diagrams.

comparison of Fig. 3(c) and (d), we find that the HRS and LRS cumulative probability of bilayer devices are more stable during 100 sweeping cycles.

In general, two models classified into "interface-type" and "filament-type" conduction path have been proposed to clarify the bipolar switching behavior. [15] The difference between them can be recognized by the cell size dependence of the HRS and LRS [15]. From Fig. 4, we observe that both HRS and LRS are insensitive to the cell size, so that the formation and rupture of the localized conduction filament is preferred as the driving mechanism of the resistance switching in the Pt/WSiO$_X$/TiN system. Besides, the linear relation between $\ln(I/T^2)$ and the square root of the applied voltage ($V^{1/2}$) indicates that the Schottky emission is the main carrier transport mechanism on HRS [12], as shown in the inset of Fig. 4. We proposed that there is a major switching area near the bottom electrode during the resistance switching process. The switching distance (∼5.1 nm) can be obtained from the slope ($q/kT\sqrt{q/4\pi\varepsilon_i d}$) of $\ln(J/T^2)$ versus the $\sqrt{V}$ plot by I–V curve fitting with the formula of Schottky emission.

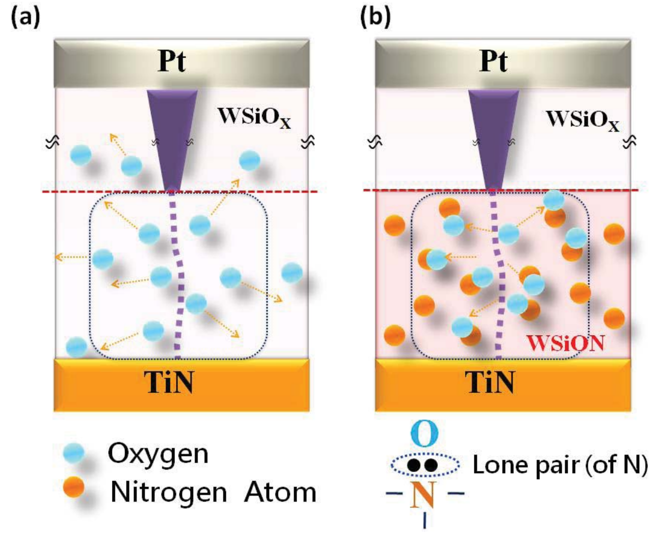

Fig. 5. Driving mechanism for the single $WSiO_X$ switching layer and double $WSiO_X$/WSiON switching layer.

During the set and reset operations, the repeated formation and rupture of the localized conduction filament accompanies the release and bonding of oxygen ions (O^{2-}) nearby the anode electrode. For single-switching-layer device, the O^{2-} is driven to bond with the filament, which disrupts the conducting path, and the random migration of O^{2-} will lead to the uncontrollable disruption length of the filament. The different disruption lengths of the filament will cause the variation in HRS. Moreover, the O^{2-} would drift away gradually from the conductive path during repeated operation [Fig. 5(a)]. Only if the O^{2-} is drifted too far to bond with the filament, the irreversible LRS will occur in RRAM devices, as shown in Fig. 1(c). In short, the switching process is the formation and rupture of the conduction path by redox reaction with oxygen; the resistance switching behavior would be improved if oxygen migration at the switching region could be controlled. Therefore, nitrogen was introduced in this letter at the proposed switch region to confine the migration of oxygen. For the $WSiO_X$/WSiON double-switching-layer device, the N-doped $WSiO_X$ layer might be able to capture and confine the released O^{2-} as shown in Fig. 5(b). The N atom can catch the oxygen atom to localize the oxygen near the conductive path. This is attributed to that the reaction speed of O^{2-} bonded with nitride is faster than oxide, as well as the bonding energy of N–O bond [indicated as lone pair in Fig. 5(b)] is higher than O–O bond [16], [17]. Thus, by introducing nitrogen, the restriction of oxygen ions' diffusion results in better property and stability of bilayer devices.

IV. CONCLUSION

In conclusion, the switching mechanism can be attributed to the formation and rupture of conduction filaments nearby the anode electrode. There is an effective switching area near the bottom electrode (TiN) during the resistance switching process. In this letter, an ultrathin WSiON layer was introduced at the $WSiO_X$/TiN interface to improve the memory working performances. The WSiON layer, as an oxygen-control layer, can confine the oxygen ion migration to enhance bipolar switching behavior. Nitrogen incorporation will improve endurance over 1000 times, which further facilitates the $WSiO_X$ RRAM application in nonvolatile memory industry.

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