Extended Abstracts of the 2006 International Conference on Solid State Devices and Materials, Yokohama, 2006, pp. 566-567

P-4-7

Low Current Reversible Resistive Switching in Bismuth Titanate Deposited by Electron Cyclotron Resonance Sputtering

Yoshito Jin, Hiroyuki Shinojima and Masaru Shimada

Microsystem Integration Laboratories, NTT Corporation,
3-1 Morinosato- Wakamiya, Atsugi, Kanagawa 243-0198, Japan
Phone: +81-46-240-2933, E-mail: jin@aecl.ntt.co.jp

1. Introduction

Reversible resistive switching between two-level or multilevel resistance states has been reported at room temperature in stacked capacitor diodes composed of insulating oxides, such as manganites,[1-6] titanates,[7-10], zirconates,[11-13] and binary metal oxides.[14-16] The resistance switching has potential for device applications, such as nonvolatile resistance random access memories. For memory applications, however, the large magnitude of current (over 10^{-2} A) in a low-resistance state (LRS) becomes a serious problem because a large-current circuit has to need to drive the memory devices. Here, we report on the properties of a bismuth titanate (BIT) thin film deposited by electron cyclotron resonance sputtering without external substrate heating. BIT has low-resistance current (around 10^{-5} A) in the LRS induced by short voltage pulses. These results indicate that BIT has a potential for memory device applications.

2. Experiments

The BIT thin film was deposited by electron cyclotron resonance (ECR) sputtering[9,10] of a Bi-Ti target in an atmosphere of Ar and oxygen. Top and bottom electrodes of Ru were also deposited by ECR sputtering on an insulating SiO_2 layer formed by thermal oxidation on a Si(100) substrate. The substrate was mounted on an electrically isolated sample holder (i.e., no external bias was applied) and heated to raise the temperature of the substrate to 300°C. The top electrodes were patterned using conventional photolithography to form pads of varies sizes, ranging from 10^2 to 10^5 μm^2. Measurements of current and voltage (*I-V*) characteristics of capacitor-like structures with the BIT thin film were performed with an impedance analyzer (Aglinet 4155C/4156C) in the dc-voltage-sweep mode as shown in Fig. 1. Multiple voltage pulses were generated with a pulse generator unit (Agilent 41501A/B).

3. Results and Discussion

Typical *I-V* characteristics of a Ru/BIT/Ru/SiO_2/Si layered structure are shown in Fig. 2. The designed film thickness of the Ru and BIT were 20 and 30 nm, respectively. BIT thin films were deposited on Ru bottom electrode by heating to 300°C and without external heating, which slightly raised the temperature of the substrate, i.e., to around 100°C due to exposure to ECR plasma stream. The bistable resistive switching with bipolar sweep of bias voltage was observed in each BIT film as follows: When the voltage was swept in the positive direction [Fig. 2(d)], the current increased, and the BIT film entered a low-resistance state (LRS). The LRS remained stable until the voltage reached the negative threshold value (typically -1 V), where the current abruptly decreased [Fig. 2(b)] by around 2 orders of magnitude and the BIT film switched to a high-resistance state (HRS). Sweeping the voltage back to the positive values [Figs. 2(d) and 2(e)] led to a sharp increase in the current, which indicated that the BIT film had switched back to the LRS. Noteworthy is that not only was the reversible resistive switching observed in the BIT film without heating, but also a very small magnitude of current (below 10^{-4} A) in the LRS was achieved in the BIT thin film deposited at low substrate temperature. Note that the switching from the HRS to the LRS occurred even when the negative bias was applied to the top electrodes as shown in Fig. 3. Similarly, switching from the LRS [Fig. 3(a)] to the HRS [Fig. 3(c)] (i.e., the unipolar sweep switching) was observed when the negative bias of -1 V was applied to top electrode. Sweeping the voltage to the negative values of -2.5 V [Fig. 3(d)] led to an increase in the current [Fig. 3(e)], indicating that the BIT film had switched from the HRS to the LRS.

Figure 4 shows the retention characteristics for each resistive state in the BIT film deposited at 300°C. Each resistive state was switched by voltage pulses. This was followed by intermittent resistance measurements at the reading voltage of -0.1 V at room temperature. The samples were kept in an 100%-nitrogen atmosphere between measurements. In the Ru/BIT/Ru/SiO_2/Si layered structure, the resistance values for the HRS and LRS were measured in different cells. Long-term retention characteristics were observed in all cells. The resistance ratio HRS/LRS (on/off ratio), exceeded three magnitudes in the structure and remained stable for the more than on week. The resistance in the HRS and LRS was around 10^8 and 10^4 Ω, respectively.

The characteristics of switching with voltage pulses are shown in Fig. 5. Ten 1-μs voltage pulses of -2.5 V were needed for switching from the LRS to the HRS. In order to return to the LRS, 500-μs current-limited pulses of -2.5 V were applied to the electrodes because the minimum pulse width became 500 μs, which is the specification of the impedance analyzer when the cut-off current is set to prevent serious damage to the sample. After each switching, we read out the resistance by applying a pulses of -0.1 V. We observed stable switching of each resistance state with over 1200 voltage pulses.

Figure 6 shows the dependence of the resistance in each state on the area of the top Ru electrode. The resistances in the HRS increase with decreasing pad area, indicating that the current flowing through the whole area of the pad is dominant. The resistance in the LRS, however, stays almost constant regardless of the pad area.

3. Conclusions

We demonstrated that reversible resistive switching occurs in

bismuth titanate thin film deposited by electron cyclotron resonance sputtering without external heating for substrate.

Acknowledgements

The authors greatly thank Drs. S. Sudo and Y. Nishida for encouragement during this work. They thank Professor Emeritus T. Shimizu of Kanazawa University for valuable discussions, and Dr. Y. Enomoto and H. Sakai for helpful advice. They also thank M. Kiuchi, T. Okubo, and A. Yokoyama of NTT-AFTY Corporation their helpful support.

References

[1] A. Asamitsu et al, Nature (London) **388** (1997) 50.
[2] A. Sawa et al, Appl. Phys. Lett. **85** (2004) 4073.
[3] T. Fujii et al, Appl. Phys. Lett. **86** (2005) 012107.
[4] S. Q. Liu et al, Appl. Phys. Lett. **76** (2000) 2749.
[5] W. W. Zhuang et al, IEDM, Tech Dig. (2004) p. 193.
[6] A. Baikalov et al, Appl. Phys. Lett. **83** (2003) 957.
[7] H. Sim et al, IEDM, Tech Dig. (2005) p. 777.
[8] Y. Jin et al, *Extended Abstracts of the 2005 International Conference on Solid State Devices and Materials* (2005) P4-14L.
[9] Y. Jin et al, Jpn. J. Appl. Phys. **45** (2006) 3243.
[10] J. R. Contreras et al, Appl. Phys. Lett. **83** (2003) 4595.
[11] A. Beck et al, Appl. Phys. Lett. **77** (2000) 139.
[12] C. Rossel et al, J. Appl. Phys. **90** (2001) 2892.
[13] Y. Watanabe et al, Appl. Phys. Lett. **78** (2001) 3738.
[14] S. Seo et al, Appl. Phys. Lett. **85** (2004) 5655.
[15] I. G. Beak et al, IEDM, Tech Dig. (2005) p. 769.
[16] A. Chen et al, IEDM, Tech Dig. (2005) p. 765

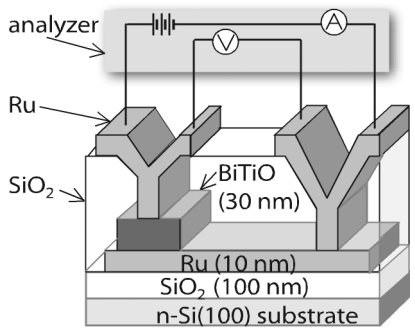

Figure 1: Schematic view of the measurement.

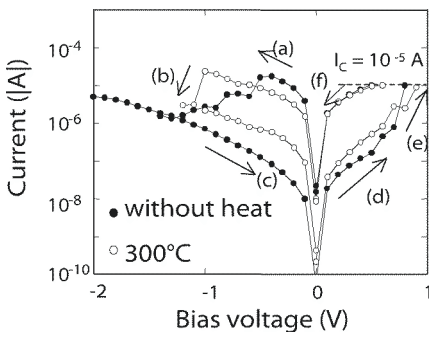

Figure 2: *I-V* characteristics (log|*I*| vs *V*) of a Ru/BIT/Ru/SiO_2/Si layered structure with bipolar sweep switching. The top Ru electrode is 220 μm^2. Deposition temperature is the parameter. Open circles: 300°C, filled circles: without heat.

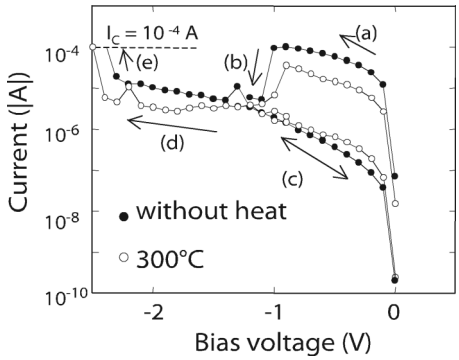

Figure 3: *I-V* characteristics of a Ru/BIT/Ru/SiO_2/Si layered structure with unipolar sweep switching. Open circles: 300°C. Filled circles: without heat.

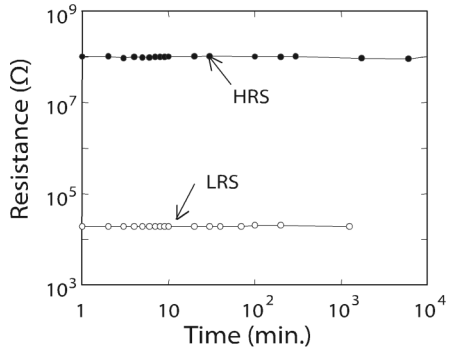

Figure 4: Retention characteristics for each resistive state in Ru/BIT/Ru/SiO_2/Si layered structure. Resistance were measured at a reading voltage of -0.1 V.

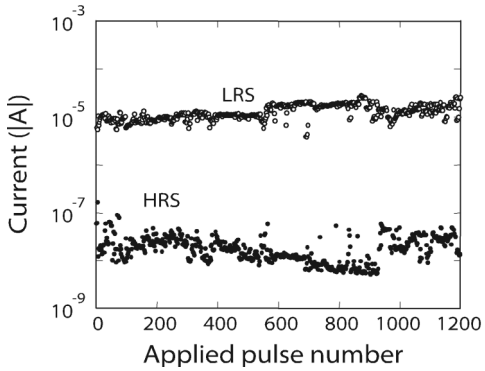

Figure 5: Switching characteristics with voltage pulses in a Ru/BIT/Ru/SiO_2/Si layered structure. The area of top Ru electrodes is 220 μm^2. Switching voltage from LRS to HRS: -2.5 V, 1 μs, 10 times. Switching voltage from HRS to LRS: -2.5 V, 500 μs, 1 time. Cut-off current from the HRS to LRS was 10^{-4} A.

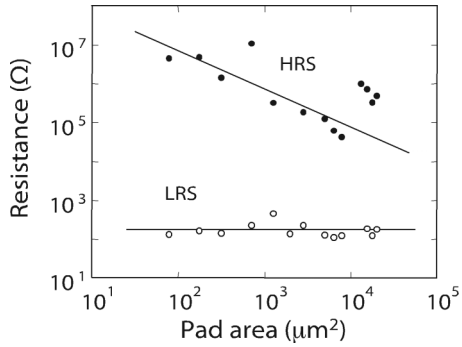

Figure 6: Pad area dependence of resistance in each state in a Ru/BIT/Ru/SiO_2/Si layered structure. Resistance was measured at a reading voltage -0.1 V.