Extended Abstracts of the 2005 International Conference on Solid State Devices and Materials, Kobe, 2005, pp.650-651

P4-14L

Reversible Resistive Switching in $Bi_4Ti_3O_{12}$ Thin Films Deposited by Electron Cyclotron Resonance Sputtering

Yoshito Jin, Hideaki Sakai, and Masaru Shimada

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

1. Introduction

The recent observation of reversible resistive switching in oxide thin films has attracted great interest due to the potential for using these films to make a new type of nonvolatile random access memory (RAM), which is often called resistance RAM [1-3]. The key feature of resistance RAM is the ability to change the resistance of an oxide film simply by applying electric pulses to it. Furthermore, the resistance remains stable under a zero bias voltage and can be read out with a small bias voltage. For memory applications, however, there remain many open questions, such as the physical mechanism and the fatigue and retention characteristics.

In this study, we have newly discovered that reversible resistive switching occurs repeatedly at room temperature in a $Bi_4Ti_3O_{12}$ (BIT) thin film simply sandwiched between bottom and top electrodes. We observed fundamental characteristics required of memory devices, such as a large on/off ratio, switching by electric pulses, and long-term retention.

2. Experiment

The BIT thin film was deposited by electron cyclotron resonance (ECR) sputtering [4] of a Bi-Ti-O target at a temperature of 450 °C in an atmosphere of Ar and O_2. The bottom electrodes, such as Pt, Ti, or Ru, were also deposited by ECR sputtering on an insulating SiO_2 layer formed by thermal oxidation on a Si(100) substrate. The top electrodes, such as Au, Pt, Ti, or Ru, were deposited by thermal evaporation or ECR sputtering and patterned using shadow masks or conventional photolithography to form squares of various sizes, ranging from about $2{\times}10^{-3}$ to $3{\times}10^{-5}$ cm^2. We fabricated a variety of capacitor-like structures with BIT thin film by changing the material of the top and bottom electrodes.

The current-voltage (I–V) characteristics were measured with an Agilent 4155C impedance analyzer operating in the dc-voltage-controlled mode as shown in Fig. 1.

3. Results and Discussion

Figure 2 shows typical I–V characteristics of a Au/BIT/Pt/Ti layered structure. The thicknesses of Pt, Ti, BIT, and Au are about 15, 15, 50, and 100 nm respectively. As-deposited BIT films have very high resistance when a small bias is applied (indicated as “initial” in Fig. 2). At a voltage of about 2.5 V, however, the resistance suddenly decreases and the BIT film enters a low-resistance state (LRS) when we finally apply about 5 V to the sample. After this process, which is like quasi-breakdown (often called “forming”), bi-stable resistive switching occurs as follows. When the voltage is swept in a negative direction [arrow (a)], the LRS remains stable until the voltage reaches the negative threshold value (typically a few volts), where the resistance abruptly increases [arrow (b)] by about five orders of magnitude and the BIT film switches to a high-resistance state (HRS). Sweeping the voltage back to the positive values [arrow (c) and (d)] leads to a sharp decrease in the resistance, which indicates the BIT film has changed back to the LRS [arrow (e)]. We cut off a large positive current (more than 1 mA) to prevent serious damage to the sample. Note that switching from the HRS to the LRS occurs even when the large negative bias is applied to the top electrode, as shown in the inset of Fig. 2. Similarly, switching from the LRS to the HRS is observed when the positive bias is applied without cutting off the positive current. Noteworthy is that the resistive switching was observed in all fabricated structures regardless of the combinations of top and bottom electrodes, though the details of I–V characteristics are slightly different.

Figure 3 shows the characteristics of switching with voltage pulses. Multiple 1-μsec voltage pulses are needed to switch from the LRS to the HRS, while current-limited pulses are needed in order to return to the LRS. After each switching, we read out the resistance by applying five reading pulses of -0.1 V. Figure 4 shows the retention characteristics for each resistive state written in different cells. So far, both cells remain stable for more than one week.

Figure 5 shows the dependence of the resistance R in each state on the area of Au top electrodes A. The resistance in the initial state and HRS largely follows the relationship of $R \propto A^{-1}$, which indicates that the current flowing through the whole area of the pad is dominant. The resistance in the LRS is, on the other hand, almost constant regardless of A. Furthermore, it hardly depends on the thickness of the BIT films (not shown here). This implies that a highly conducting path with a finite size is formed between electrodes in the LRS, where the contact resistance at the interface can be dominant. Such a filament may be somehow related to the defects generated during the forming process. The resistive switching after that is naturally considered to be caused by the creation and annihilation of the conducting path. Details of the mechanism, however, are still unclear.

4. Conclusions

We have found reversible resistive switching occurs in a $Bi_4Ti_3O_{12}$ thin film deposited by electron cyclotron resonance sputtering. The on/off ratio is up to five orders of magnitude. Reversible switching with voltage pulses and long-term retention were observed. From the conduction characteristics in the low resistance state, the most plausible explanation of switching is the formation and annihilation of highly conducting filaments.

Acknowledgements

The authors wish to thank Dr. Y. Enomoto for helpful advice and fruitful discussion.

References

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

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

[3] S. Seo, M. J. Lee, D. H. Seo, E. J. Jeoung, D.-S. Suh, Y. S. Joung, K. Yoo, I. R. Hwang, S. H. Kim, I. S. Byun, J.-S. Kim, J. S. Choi, and B. H. Park, Appl. Phys. Lett. **85**, 5655 (2004).

[4] T. Ono, H. Nishimura, M. Shimada, and S. Matsuo, J. Vac. Sci. Technol. A **12**, 1281 (1994).

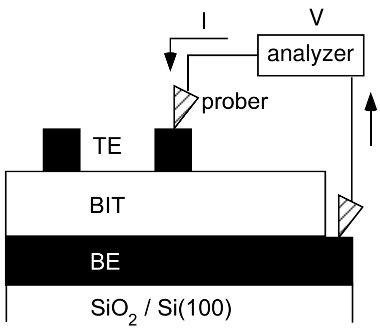

Figure 1: Schematic view of measurement. TE, BIT, and BE are the top electrode, $Bi_4Ti_3O_{12}$ and the bottom electrode, respectively.

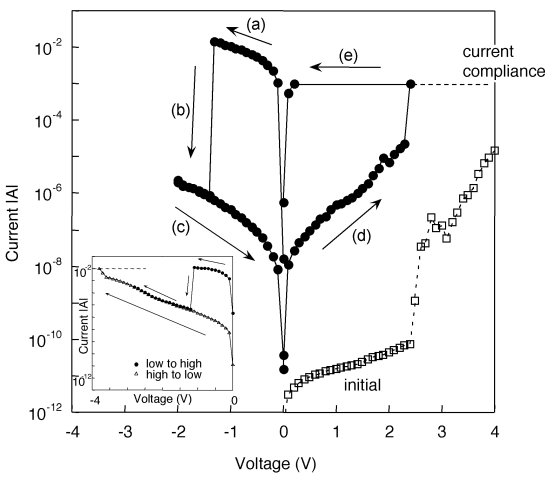

Figure 2: I–V characteristics (log$|I|$ vs V) of a Au/BIT/Pt/Ti layered structure with arrows indicating the sweep direction. The top Au electrode is 6.0×10^{-5} cm^2. Inset shows the ability to switch back to the LRS with negative bias voltages.

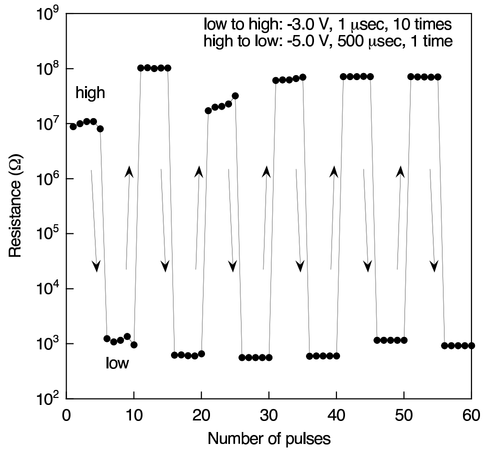

Figure 3: Switching characteristics with voltage pulses in a Au/BIT/Pt/Ti layered structure. The top Au electrode is 1.0×10^{-4} cm^2. After each switching, five reading pulses (-0.1 V) were applied.

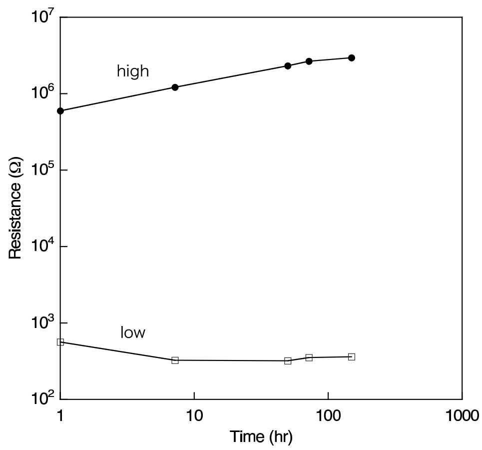

Figure 4: Retention characteristics for each resistive state in a Ru/BIT/Pt/Ti layered structure. Resistance was measured at a reading voltage of -0.1 V. The top Ru electrode is 3.9×10^{-5} cm^2.

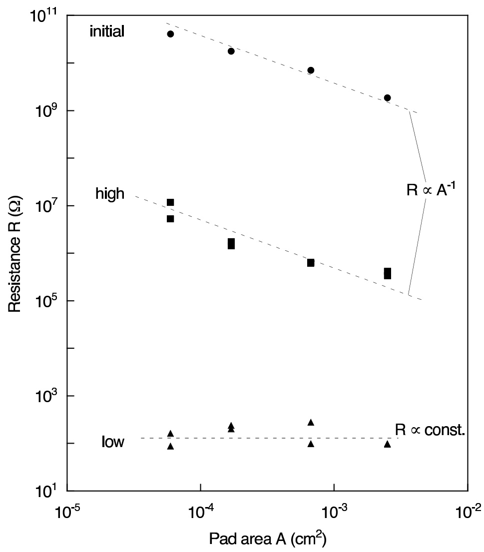

Figure 5: Pad area dependence of resistance in each state in a Au/BIT/Pt/Ti layered structure. Resistance was measured at a reading voltage of -0.1 V.