Resistance Switching in Bismuth Titanate Thin Film for Resistance Random Access Memory

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Abstract

Reversible resistance switching has been observed in bismuth titanate thin film deposited by electron cyclotron resonance sputtering. The film exhibits bipolar-sweep and unipolar-sweep switching. The resistance ratio of the high- and low-resistance states is as high as four orders of magnitude. Voltage pulses drive reversible resistive switching and the retention time is several months. Bismuth titanate film has good potential for application to memory devices.

1. Introduction

Nonvolatile memory (NVM) products include memory cards for digital cameras, USB (universal serial bus) flash drives (also called thumb drives etc.), contactless IC cards, multifunctional cellular telephones, personal digital appliances (PDAs), and portable digital music players. These memory devices have infiltrated our lives and fundamentally changed the way we live, something that was unimaginable just a decade ago. Furthermore, NVM is sure to play an important role in the ubiquitous services of the near future.

Most NVMs on the market use flash memory, which is an improved version of electrically erasable programmable read-only memory (EEPROM). It comes in two types, NAND and NOR, depending on the structure of the storage cell. A positive growth cycle of technical improvement and economic efficiency has led to steady market growth for flash memory. New applications have been generated and market expansion has been driven by the reduced device prices afforded by ultralarge-scale integration, and profits have been reinvested into research and development of even more-advanced devices. However, it will be difficult to maintain such a positive growth cycle because we will soon reach the limit of miniaturization. Moreover, memory cells in flash memory consume a large amount of electric power when data is written and are relatively slow because of the poor writing speed of this method. (You may have noticed that USB memory gets hot while you wait for it to write large amounts of data.) Therefore, it is doubtful that flash memory will be suitable for ubiquitous services, which will involve vast amounts of data.

To overcome the spatial and functional limitations imposed on conventional semiconductor devices based on charge storage, many laboratories are aggressively studying the next generation of NVMs, such as ferroelectric random access memory (FeRAM) [1], [2], magnetoresistive random access memory (MRAM) [3], phase change random access memory (PRAM)[4], and resistance random access memory (ReRAM) [5]-[8]. The mass production of small-scale FeRAM devices has already started, and that of MRAM will start in the near future. PRAM is attractive because of its low cost. ReRAM promises high-density integration because of its simple basic structure. It also offers high-speed and low-power operation because the resistance of an oxide film can be changed by applying a small voltage of electrical pulses to an interelectrode. The characteristics of each type of NVM are summarized in **Table 1**, together with the characteristics of dynamic random access memory (DRAM), which is a volatile form of memory widely used in computers.

The basic structure of ReRAM is a metal-oxide-metal structure, as shown in **Fig. 1(a)**. When voltage pulses are applied through the electrodes, the resis-

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Table 1. Features of ReRAM, FeRAM, MRAM, PRAM, Flash memory, and DRAM.

	ReRAM	FeRAM	MRAM	PRAM	Flash memory (EEPROM)	DRAM
Cell size	$4F^2$~$10F^2$	$6F^2$~$12F^2$	$6F^2$~$12F^2$	$6F^2$~$12F^2$	$6F^2$~$12F^2$	$6F^2$~$12F^2$
Nonvolatile	yes	yes	yes	yes	yes	no
Writing voltage	1~5 V	2 V	3 V	3 V	12 V	3 V
Reading voltage	0.1 V	1 V	2 V	1 V	2 V	0.5 V
Multilevel	yes	no	no	no	yes	no
Repeatability	unknown	10^{12}	10^{16}	10^8	10^6	10^{16}

F: minimum feature size

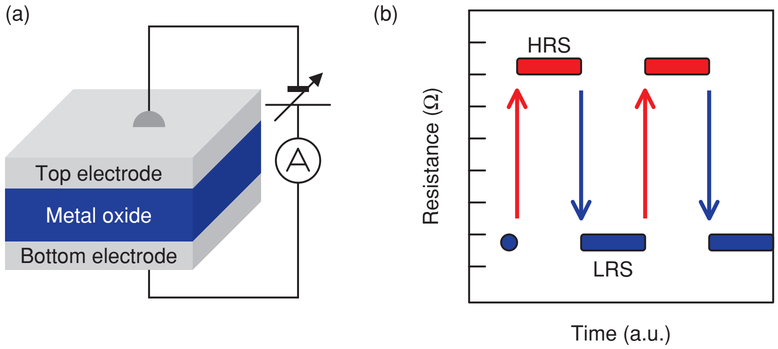

Fig. 1. (a) Basic structure of ReRAM and (b) RRS characteristics.

tance of the metal oxide switches between a high-resistance state (HRS) and low-resistance state (LRS), as shown in **Fig. 1(b)**. We call this reversible resistance switching (RRS)*. HRS and LRS both exhibit long-term state retention and their resistance ratio is several orders of magnitude. The resistance state of the oxide film can be read out by applying a small reading voltage to the electrodes. However, there are several remaining issues that need to be addressed such as reliability, adjustability for device fabrication, and clarification of the switching mechanism.

Our group has been investigating bismuth titanate (BIT) deposited by electron cyclotron resonance (ECR) for RRS. In this article, I show that RRS occurs repeatedly at room temperature in a BIT film sandwiched between electrodes and that the film has the fundamental characteristics required of a memory device, such as a large on/off ratio, switching by electric pulses, and long-term state retention.

2. Experimental procedure

Thin BIT films were deposited by ECR sputtering [9]-[11]. The ECR sputtering system is schematically illustrated in **Fig. 2**. An advanced plasma source

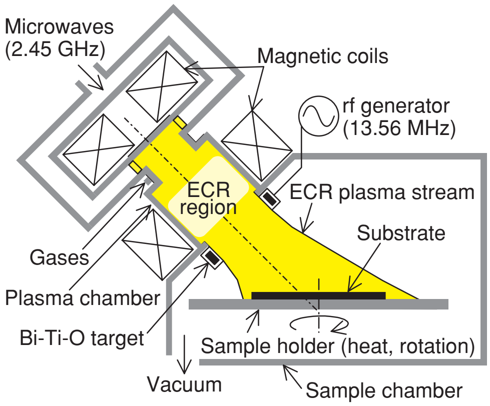

Fig. 2. Schematic diagram of the apparatus for ECR sputtering deposition.

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* Reversible resistance switching: repeatable state changes between two or more resistance levels in response to an external electric bias. This phenomenon is known by various alternative names, such as colossal electroresistance (CMR), reversible resistive switching, cyclic repetitive resistance switching, and reproducible resistance switching.

was used. A cylindrical Bi-Ti-O target (Bi:Ti = 4:3, 99.99%) was placed between the plasma and sample chambers. Argon and oxygen were introduced into the plasma and sample chambers, respectively, at rates sufficient to produce a pressure of 1.0×10^{-2} Pa. Microwaves with a frequency of 2.45 GHz and magnetic flux with a density of 87.5 mT constituted the ECR conditions for plasma generation. The Bi-Ti-O target was biased by a radio-frequency (rf) field (13.56 MHz) and then sputtered by ions in the ECR plasma stream. The substrate was mounted on an electrically isolated sample holder, i.e., no external bias was applied, and heated to 450°C. When the BIT film was deposited on a 150-mm-diameter Si wafer, the average deposition rate was 3.56 nm/min, and the refractive index of the film was 2.516, which corresponds to the refractive index value of BIT film deposited by rf magnetron sputtering [12]. To improve the uniformity of the thickness of the deposited films, the substrate was inclined to the target at an angle of about 30° and rotated at 15 rpm [10], [11]. As a result, excellent uniformity was obtained: the variations in the deposition rate and refractive index were within ±0.77% and ±0.22%, respectively.

The bottom electrodes, Pt/Ti and Ru thin film, were also deposited by ECR sputtering on an insulating 100-nm-thick SiO_2 layer formed by thermal oxidation on a Si (100) substrate. The top electrodes, Au and Ru thin film, were deposited by thermal evaporation of a gold ingot into the vacuum or by ECR sputtering and patterned using shadow masks or conventional photolithography to form squares of various sizes ranging from 2×10^{-7} to 3×10^{-9} m^2.

Current and voltage (*I-V*) characteristics were measured with an Agilent 4155C/4156C impedance analyzer in the dc-voltage-controlled mode. Multiple voltage pulses were generated with an Agilent 41501A/B pulse generator unit. The thicknesses and refractive indices of BIT films were measured by ellipsometry with 632.8-nm light.

3. Results and discussion

Typical *I-V* characteristics of a Au/BIT/Pt/Ti/SiO_2/Si layered structure are shown in **Fig. 3**. The top Au electrodes, BIT, and bottom electrodes (Pt/Ti) were stacked on the SiO_2/Si substrate and the bias voltage was applied between the top and bottom electrodes. The top Au electrode was 6.0×10^{-9} m^2. The designed film thicknesses of Pt, Ti, BIT, and Au were 15, 15, 50, and 100 nm, respectively. BIT films just after the deposition had very high resistance when a small bias was applied, indicated as "initial" in Fig. 3(a). At around 2.5 V, however, the current suddenly increased, and the resistance state in the film changed to LRS when we finally applied about 5 V, which is called the "forming" process [8], indicated as "forming" in Fig. 3. After the forming process, the resistance-switching phenomenon was observed. The resistance state in the film could be switched by applying a bias of the opposite polarity (bipolar-sweep switching) or the same polarity (unipolar-sweep switching) to the interelectrode.

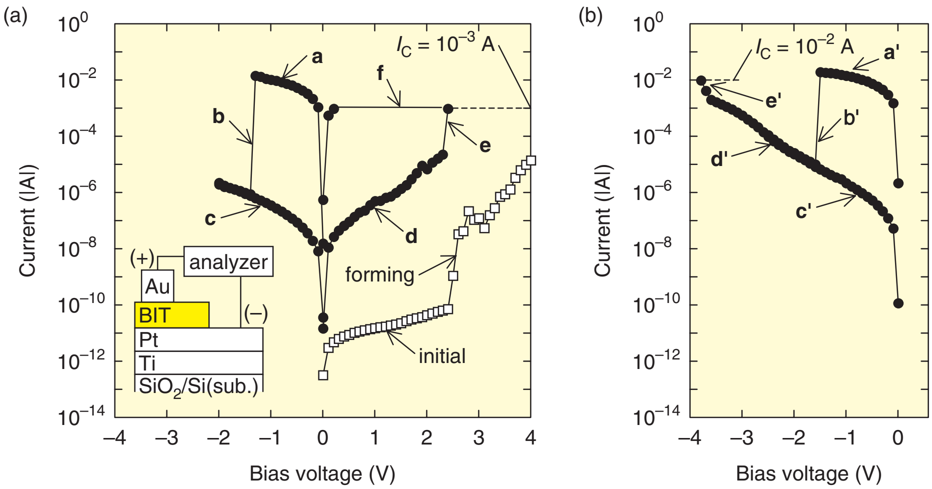

Fig. 3. *I-V* characteristics (log *I* vs. *V*) of a Au/BIT/Pt/Ti/SiO_2/Si layered structure. Open squares: initial sweep. (a): Bipolar-sweep switching. (b): Unipolar-sweep switching. The inset is a schematic view of the measurement. I_c is the cut-off current during measurement.

Bipolar-sweep switching was observed, as shown in Fig. 3(a). When the voltage was swept in the negative direction (sweep **a**), the resistance state in the LRS remained until the voltage reached the negative threshold value (typically a few volts), where the current abruptly decreased (sweep **b**) by around four orders of magnitude and the resistance state of the film switched to HRS. Sweeping the voltage back to positive values (sweeps **c** and **d**) led to an abrupt increase in the current, which indicated that the resistance state in the film had switched back to LRS (sweep **e**). Large positive currents of more than 1 mA were cut off (cut-off current I_c) to prevent serious damage to the sample, as shown in Fig. 3(a).

We observed unipolar-sweep switching when a negative bias was applied to the top electrode, as shown in Fig. 3(b). When the voltage was swept in the negative direction (sweep **a'**), the resistance state in the LRS remained until the voltage reached the negative threshold value (around –2.0 V), where the current abruptly decreased (sweep **b'**) and the resistance state in the film switched to HRS (sweep **c'**). Sweeping the voltage to negative values (sweep **d'**) led to an increase in the current (sweep **e'**), indicating that the resistance state in the film had switched from HRS to LRS. When the negative bias was applied to the top electrode again, the resistance state in the LRS was observed (sweep **a'**).

Note that the resistance switching was observed in various structures regardless of the combinations of top and bottom electrodes, such as Au/BIT/Pt/Ti/SiO_2/Si, Au/BIT/Ru/SiO_2/Si, or Ru/BIT/Ru/SiO_2/Si layered structures. The retention characteristics for each resistance state in the Ru/BIT/Ru/SiO_2/Si layered structure are shown in **Fig. 4**. The top Ru electrode was 4×10^{-10} m^2. The BIT film was deposited at 450°C.The resistance states in both HRS and LRS were switched by applying voltage pulses and the resistance values for HRS and LRS were measured in different cells. The samples were kept in a 100%-nitrogen atmosphere between measurements. Intermittent resistance measurements were performed at a reading voltage of –0.1 V at room temperature. Long-term retention characteristics were observed in all cells. The resistance ratio of HRS to LRS, i.e., the on/off ratio, was as high as two orders of magnitude in the structure and remained stable for several months.

Figure 5 shows the switching characteristics for various voltage pulses for each resistance state in a Au/BIT/Pt/Ti/SiO_2/Si layered structure. The area of the top Au electrode was 1×10^{-8} m^2. Ten 1-μs pulses of –3.0 V were needed for switching from LRS to HRS. After switching to HRS, we read out the resistance five times by applying a reading pulse of –0.1 V, indicated by closed circles in Fig. 5. To return to LRS, a single 500-μs current-limited pulse of –5.0 V was applied to the top electrode because the minimum pulse width was 500 μs, which is the specification of the impedance analyzer when the cut-off current is set to prevent serious damage to the sample: here, the cut-off current from HRS to LRS was 1 mA. Then we read out the resistance five times by applying a reading pulse of –0.1 V, indicated by open circles in Fig. 5. We observed stable switching of each resistance state with these voltage pulses.

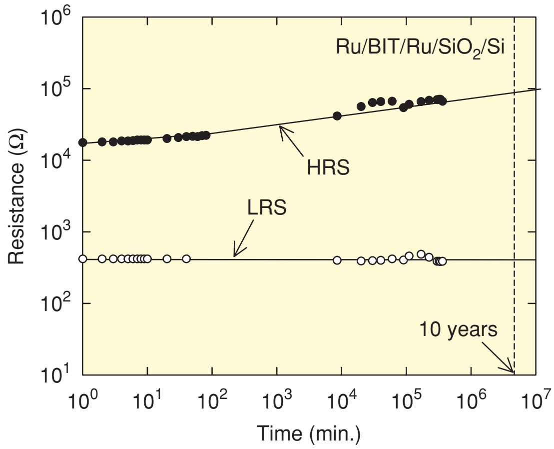

Fig. 4. Retention characteristics for each resistive state in the Ru/BIT/Ru/SiO_2/Si layered structure. Closed circles: current in HRS. Open circles: current in LRS.

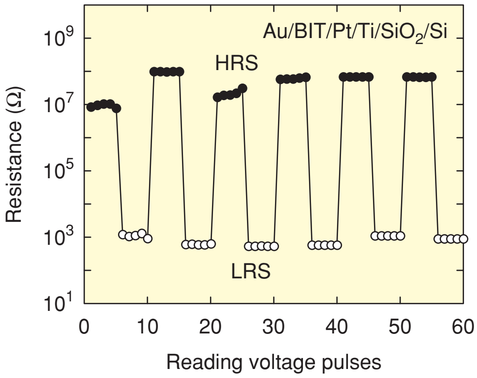

Fig. 5. Switching characteristics with voltage pulses in the Au/BIT/Pt/Ti/SiO_2/Si layered structure. Closed circles: resistance in HRS. Open circles: resistance in LRS.

4. Summary

Reversible resistive switching in bismuth titanate thin film deposited by electron cyclotron resonance sputtering has been demonstrated. The film exhibits bipolar and unipolar sweep resistance switching. The resistance ratio of the high- and low-resistance states was up to four orders of magnitude. Voltage-pulse-driven reversible resistive switching and long-term state retention of several months were observed. BIT film has characteristics that make it applicable to memory devices.

Acknowledgment

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