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I-V measurement of $Pr_{0.7}Ca_{0.3}MnO_3$ during TEM observation

Takashi Fujii, Hiromichi Kaji, Hirofumi Kondou, Kouichi Hamada, Masashi Arita and Yasuo Takahashi

Graduate School of Information Science and Technology, Hokkaido University,
Kita14 Nishi9, Kita-ku, Sapporo 060-0814, Japan
Phone : +81-11-706-6457 E-mail : t-fujii@ist.hokudai.ac.jp

1. Introduction

$Pr_{0.7}Ca_{0.3}MnO_3$(PCMO) which is a perovskite-type oxide shows large resistance change induced by voltage pulses[1]. This phenomenon can be applied to the nonvolatile memory named as a resistance random access memory (ReRAM). ReRAM has high functionality such as large resistance change and high speed access. Therefore, ReRAM is expected to be a nonvolatile memory of the next generation.

However, the physical mechanism of this resistance switch is not yet clearly understood. In some oxide, filament-like current path are believed to be formed and they are related to this resistance change [2]. As another model, some studies maintain that the oxygen vacancy plays important role in resistance change [3]. Based on these models the microstructures inside the oxide may change during the resistance switch.

Whatever the switching mechanism is, the structural observation in nanoscale during the resistance switch must give important information to interpret the mechanism.

In this work, therefore, the current-voltage (I-V) measurements and transmission microscopy (TEM) observations were simultaneously performed. As a result no remarkable changes inside PCMO such as the formation of conducting path were recognized.

2. Experimental

The TEM observation system is as follows. A custom-made TEM sample holder (Fig. 1) was attached to a TEM instrument (JEOL JEN2010 Cs=0.5mm). Two tip-shaped electrodes are attached to the holder. One of them was made of Pr-Ir and was covered by a PCMO layers. Another electrode tip was made of W and was movable. It was used as the counter electrode for the I-V measurement after selecting positions to be measured during TEM observation. The position control of the W-electrode was performed by using piezo control software developed by the present authors. In the conduction measurement, there are some circuit lines and the I-V measurements were performed using a source-meter (Yokogawa GS610). The TEM images were recorded using a CCD video camera. The synchronization between the TEM image and the I-V data were performed by the human voice recorded in the video system.

To obtain I-V data from nano-regions, very sharp counter electrodes should be used, of which the apex size is several tens of nanometer or less. For this purpose tungsten were sputtered using the ion shadow method after the electrolytic polishing. A scanning electron microscopy (SEM) image of the W electrode is shown in Fig. 2. The Pt-Ir electrode on which the thin PCMO film is deposited should be wide and thin to perform plural investigations in one batch. The commercially available scanning tunnel microscopy (STM) tip made of Pt-Ir was mechanically ground into a wedge shape. Afterward, it was polished by the ion milling method. An example is shown in Fig. 3. The electrode was about 50μm wide and thin enough for TEM observations. On this wedge shaped electrode, the PCMO was deposited by rf sputtering of $Pr_{0.7}Ca_{0.3}MnO_3$ ceramic target. The gas flow and the vacuum during the sputtering was Ar/O_2 18/2 SCCM, and 0.6 Pa, respectively. The deposition of PCMO was performed at 800°C.

3. Result and discussion

A TEM image during the approach of the electrode is shown in Fig. 4. The polycrystalline PCMO layer deposited on the Pt-Ir tip was 5~10nm thick. The W electrode was moved along the arrow and it was touched to PCMO. The contact area was about 30 nm^2 or less, assuming a circular contact. The I-V curve from this region is presented in Fig. 5. It is a hysteresis curve characteristic in ReRAM. The resistance was changed from the low resistance state (LRS) to the high resistance state at about +2V. It was back to the LRS at about of -2V. The TEM images of the PCMO crystal before and after the measurement are compared in Fig. 6. We didn’t confirm signs where the conducting path like the filament had been formed. From these TEM images, it is thought that the resistance change of PCMO is not due to the filament formation. In addition, no remarkable structure change in PCMO is recognized.

There is a model to explain the switching mechanism of perovskite-type oxides, where oxygen defects at the interface between the oxide and the electrode are related to the resistance change [3]. Based on this model, the amount of oxygen defects increased or decreased by the changing in voltage polarity. Relating to this, the movement of a large number of oxygen ions might be induced in the PCMO crystal. If such an oxygen movement influences the resistance change, the nano structure change may occur in the PCMO lattice. Under the above assumption, structure change in PCMO is so slight to be recognized. For further discussions in detail high resolution TEM observation during resistance switch should be concentrated on the interface between PCMO and the electrode.

4. Summary and Conclusion

We observed PCMO in TEM with simultaneous I-V measurements. The characteristic resistance change, phenomenon was realized in the TEM. Comparing images taken before and after the resistance change, it was summarized that no conducting path was formed in this sample. No remarkable crystallographic structure change was seen. From these results, it is thought that no or very faint change occurred in the PCMO lattice. The model in ref.3, where the oxygen defects at PCMO-electrode interface takes part in the resistance change, is one of the possibility model to explain the switching mechanism in the ReRAM made of PCMO.

Acknowledgements

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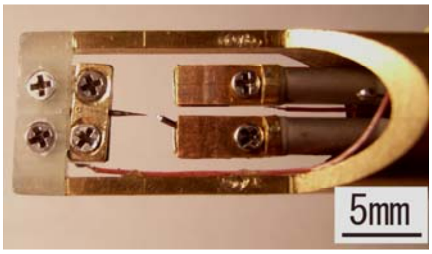

Fig. 1. Custom-made TEM holder.

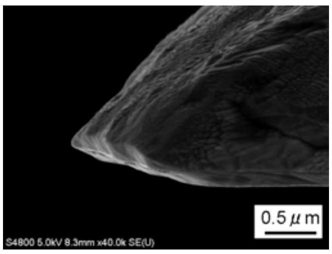

Fig. 2. SEM image of the W tip.

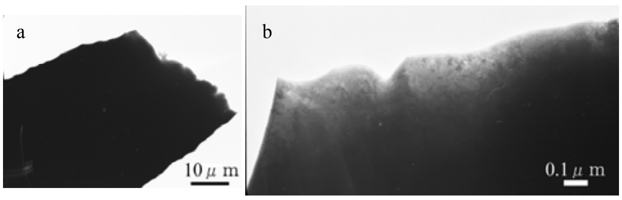

Fig. 3. (a) TEM image of Pt-Ir tip and (b) enlarged image at the edge.

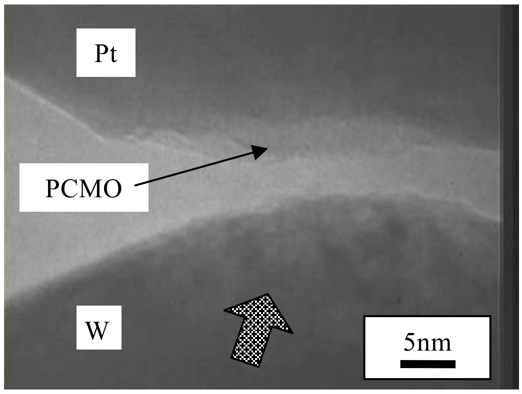

Fig. 4. TEM image of the W electrode approaching to Pt-Ir covered PCMO

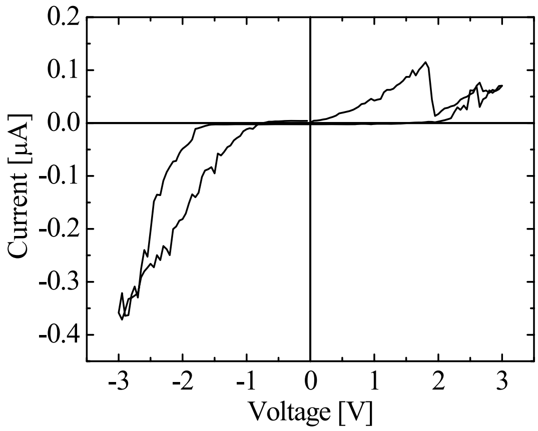

Fig. 5. I-V measurement showing hysteresis.

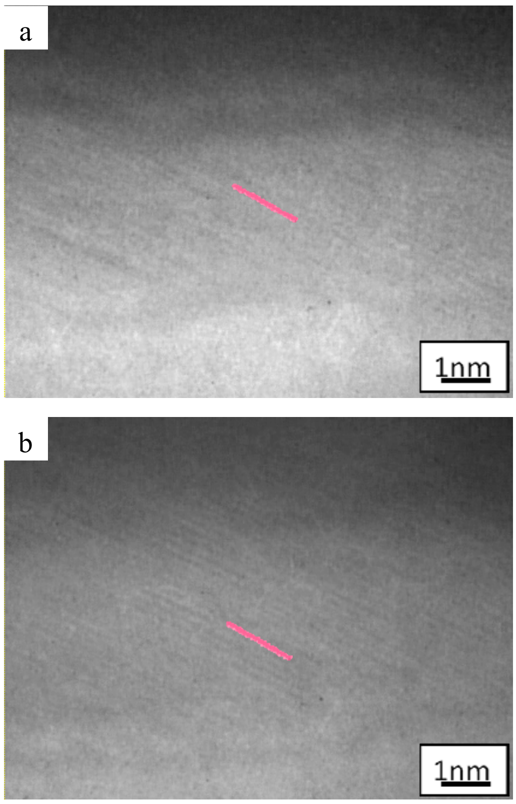

Fig. 6. TEM image of PCMO (a)before and (b) after the measurement.