

Voltage-induced insulator-metal transition at room temperature in an anodic porous alumina thin film

S. Kato¹, S. Nigo², Y. Uno², T. Onisi² and G. Kido¹

¹National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan

²Limited Company Misuzu R&D, 2-6-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan

KATO.Seiichi@nims.go.jp

Abstract. Bistable switching effect, induced by an electric field, in an anodic porous alumina thin film is reported. An electrode was bonded on the surface of a thin film with Ag paste, and I-V characteristic between the electrode and the aluminium substrate was measured. The I-V characteristic reveals a reversible resistance change, initiating at +4 V and terminating at -1.5 V at room temperature. Huge electrical resistance change ratio (RR), defined as the ratio of the resistance change to the low resistance state, is observed. The RR is approximately ten million. The resistance in the low resistance state was measured down to 18 K. The temperature dependence of the resistance shows a metal-like behaviour. The huge RR and the temperature dependence of the resistance suggest that an insulator-metal transition is occurred. Excellences of this device are huge RR ratio, easiness of mass production, and containing only common materials. It is a promising material for non-volatile memory with low power consumption and other electrical applications.

1. Introduction

Anodic porous alumina has nanometer-sized uniform holes arranged in a honeycomb structure, and is of great interest as a key material for fabrication of nano-devices [1-5]. The process of fabricating porous alumina is simple and economical compared to commonly-used high-vacuum processes, and easily provides samples with a large area. We have investigated electrical properties of porous alumina and found a voltage-induced bistable switching effect with huge electrical resistance change ratio (RR), which is defined as the ratio of the resistance change to the low resistance state [6]. Large RR is desirable for application to nonvolatile memory with low power consumption, and porous alumina is a promising material. In this paper, details of the switching effect and a low temperature measurement of resistance are reported.

2. Experimental

An anodized porous alumina thin film was prepared by a two-step anodization process [1]. The surface of an Al sheet (99.99% 1mm thickness) was treated with chemical mechanical polishing (roughness <10 nm), and electrical polishing in a solution of perchloric acid and ethanol. The Al sheet was anodized at a constant voltage of 40 V in a 0.3 M oxalic acid solution at 20 °C for 3 hours. Then the anodic oxide layer was removed in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 60 °C over 6 hours. Subsequently, the Al sheet was anodized again for 2 minutes under the same

conditions as in the first step. The upper electrode, consisting of a Ag contact pad 1mm in diameter, was formed with Ag paste (Pyro-Duct supplied by Nilaco) and dried at 95 °C for 1 hour in a vacuum oven.

The anodized aluminum sheet was sliced in a vertical direction to the surface by a focused ion beam (FIB). A slice of the sample was observed with TEM at 300 kV. The thickness of the specimen was 150 nm. The surface of the thin film was observed with SEM.

The measurement of the I-V characteristic was carried out with an I-V analyzer at room temperature. Figure 1 shows a schematic circuit diagram of the system for the I-V characteristic measurement. A fixed resistance of 100 Ω was inserted in series with the measuring circuit to prevent the element from being destroyed by an over-current. The sweep range was ±5 or 6 V, and the sweep speed and the step size were, 500 mV/sec and 100 mV, respectively. Temperature dependence of resistance was also measured. After increasing the voltage to +6 V, it was decrease to +2 V, and then electric current was measured down to 18 K with keeping the voltage at +2 V. The resistance was calculated from the electric current.

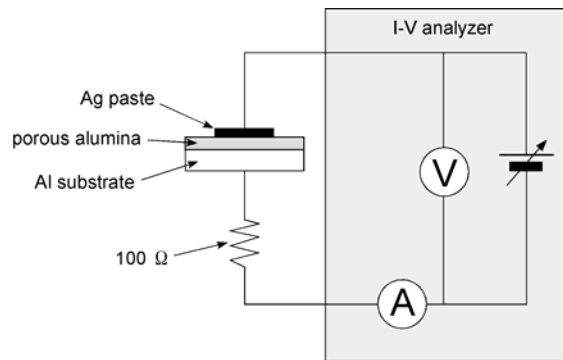


Fig. 1 A schematic of the measuring circuit for I-V characteristic of the memory.

3. Results and discussions

Figure 2 (a) shows a SEM image of the surface of the thin film. Nano holes 30 nm in diameter are arranged in a highly ordered honeycomb type structure. The spacing between nearest holes is 100 nm. Figure 2 (b) shows a cross section TEM image of the thin film. The thickness of the alumina film is 200 nm. No visible cracks are observed in the alumina.

The I-V characteristic depends on samples. About 20% of samples show hysteresis I-V curves. We guess it is caused by adhesion failure of electrodes. Figure 3 (a) displays the measured I-V curves of sample No. 20 with the protective resistance. The measurement was performed with 10 cycles. The I-V curve proceeds from 'a' to 'g' in each cycle. Bistable switching is observed in the I-V curve, initiating between +3.5 and +4.5 V, and terminating between -1.5 and -2.5 V. An on/off change doesn't occur at intermediate voltages. The section of the I-V curve crossing the 0 V point is linear. We tried the same measurement after 10 days with the sample in ON and OFF states, and confirmed that the states had persisted. Resistance of a sample is calculated from current and voltage. The resistance of sample No. 18 vs. applied voltage is shown in fig. 3 (b). The electrical resistance change ratio, $\Delta R/R_{on}$, is defined as

$$\frac{\Delta R}{R_{on}} = \frac{R_{off} - R_{on}}{R_{on}},$$

where R_{on} and R_{off} are the electrical resistances of the low and high resistance states, respectively. The $\Delta R/R_{on}$ of the sample is 11,000,000. As mentioned above, it is desirable for the ratio to be large for

applications to nonvolatile memory so that be it is possible to read on/off states with low power consumption. Several materials with large RR have been reported. Hayakawa et al. have reported that CoFeB/MgO/CoFeB junctions, in which switching is induced by magnetic fields, have an RR of 2.60 at room temperature and 4.03 at 5 K [7]. Liu et al. have reported electric-pulse-induced switching in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ with an RR of 17 at room temperature [8]. Our value of 11,000,000 is more than 600,000 times larger.

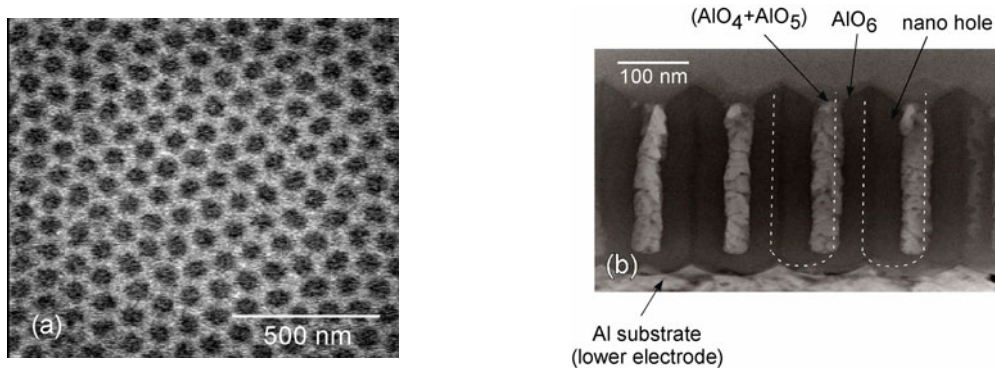


Fig. 2 Electron microscope images of aluminum duplex oxide film fabricated by anodization. (a) SEM image of a surface with a nano-hole honeycomb array. (b) Cross-sectional TEM image shows the nano-hole and multi-layers of duplex AlO_x . AlO_x forms amorphous duplex oxide layer. The outer layer is of AlO_6 . The inner layer is of AlO_5 and AlO_4 .

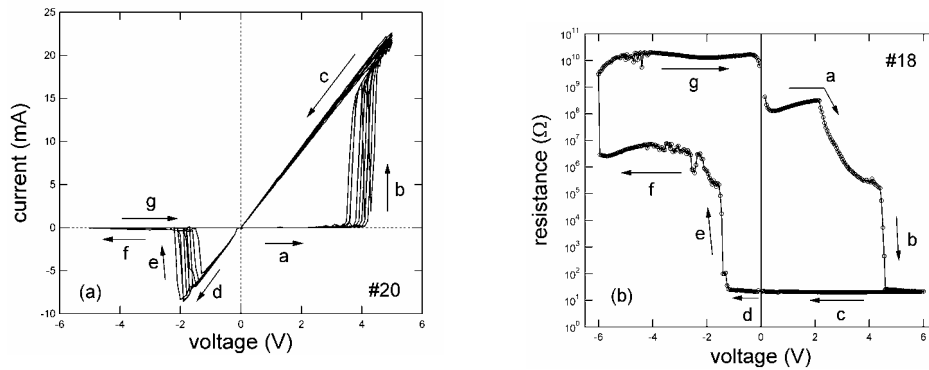


Fig. 3 (a) Ten cycles hysteresis I-V curves of sample No. 20 and (b) resistance vs. applied voltage of sample No. 18. Both curves proceed from 'a' to 'g'.

Figure 4 displays temperature dependence of resistance down to 18 K of another sample. The resistance shows a linear decrease with temperature decrease. The behavior is similar to metal behavior. The huge RR and the behavior of resistance suggest that an insulator-metal transition is occurred.

^{27}Al multiple-quantum magic-angle-spinning (MQMAS) and MAS NMR measurements using 930 MHz NMR at NIMS have revealed that porous alumina consists of duplex amorphous oxide layers [9-11]. The main constituents of the inner and outer oxide layers are $[\text{AlO}_4]$ and $[\text{AlO}_5]$ and $[\text{AlO}_6]$ as indicated in Fig. 2 (b). The electronic states are complicated because of the concentration gradient of oxygen ions and the difference of the valence of aluminum ions. When the applied voltage increases over a threshold voltage, electrons which are trapped in the AlO_x layers may transform the electronic states into metal-like electronic states. Further investigation is necessary for understanding this effect.

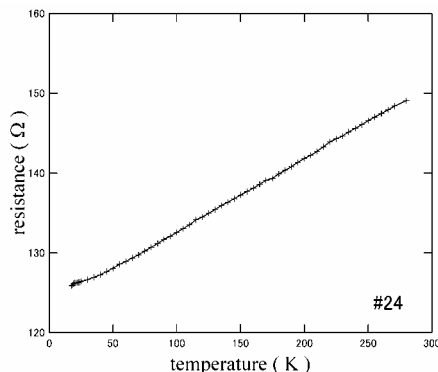


Fig. 4 Temperature dependence of electrical resistance of sample No. 24.

4. Conclusion

We have found a bistable switching effect in anodic porous alumina thin film. The effect is induced by electric fields and achieve an RR of ten million or more. The huge RR and the temperature dependence of the resistance suggest that insulator-metal transition is occurred. No poisonous and/or expensive materials are necessary for the production of the material. Consequently, we believe anodic porous alumina is a promising material for high performance nonvolatile memory and other electronic applications.

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