Transport Properties of Anodic Porous Alumina for ReRAM

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Abstract: A voltage-induced bistable switching effect has been studied for M/AlOx/Al devices made of the anodic porous alumina with a top electrode of aluminium (or silver) to develop a next generation memory (AlOx-ReRAM). The resistance state of memory is switched between OFF-state (high resistance) and ON-state (low resistance), where the resistance ratio is higher than 10^4. In the thermally stimulated current (TSC) measurement, a narrow band was observed around 290 K, indicating the conduction mechanism comes from a kind of impurity band in the energy gap. An anomaly was also observed around 290 K in the temperature dependence of resistance at the ON-state.

1. Introduction
Recently, resistive random access memory (ReRAM) has much attracted great interest for the application in the next generation memory with high-speed, high density and nonvolatile properties. Various nanomaterials are investigated for an application of ReRAM, and candidate materials are generally thought to be doped perovskite and/or transition metal oxide. Anodic aluminium oxide (AAO) is of great interest as a key material for fabrication nano-devices. Transport properties of AAO with nano-wires of various materials in the nano-holes are investigated [1, 2], and switching effect was reported [1]. We have investigated AAO with nothing in the holes and reported that AAO with nanometer-sized uniform holes arranged in a honeycomb structure shows reversible switching phenomena [3]. The electrical state is changed between “low resistance” (ON state) and “high resistance” (OFF state) by applying a small voltage between the top electrode (attached to the surface of the thin film) and the bottom electrode (aluminum substrate). Since the switching was reproducible at room temperature, the AAO cell can be used as a non-volatile memory. In addition, the porous alumina thin film consists of only aluminum and oxygen, which are harmless and abundant in the earth, and a large scale integrated memory can be produced in a simple processes at low cost. In order to investigate the conduction mechanism through the porous layer, the structures of the material of the AAO cell were studied by very high-field solid-state NMR spectrometer (21.8 T) as well as TEM, SEM, X-ray diffraction. The results showed that the porous part consists of amorphous alumina with much oxygen vacancy [3, 4]. The principle of operation of the switching effect is, however, not yet clear, and we have measured the temperature dependence of the AAO memory cell and the thermally stimulated current (TSC). We have also fabricated anodic porous alumina on a silicon substrate aiming to make a prototype of an aluminum oxide resistive random access memory (AlOx-ReRAM).
2. Switching characteristic

The AAO memory cell was prepared by the following procedure. An anodized porous alumina thin film was prepared by a two-step anodization process [5]. The surface of an Al sheet (99.999%, 0.5 mm thickness) was electrically polished 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 chromium oxide at 60°C in 15 minutes. Subsequently, the Al sheet was anodized again for 1 minute under the same conditions as in the first step. The upper electrode was formed with aluminum (or silver) vapor deposition. Resistance change of the AAO cell was measured at room temperature with a semiconductor characterization system (Keithley 4200-SCS) as shown in fig. 1a. Applied electric pulses were ±9 V in voltage and 10 ms in duration. Electric resistance was measured after each ±9 V pulse. The applied pulse pattern and resistance vs. switching cycle number are indicated in fig. 1b and fig. 1c, respectively. Clear non-volatile resistance change induced by electric pulse was observed. The resistance ratio between the high-resistance state and the low-resistance state is higher than 10^4. This value is higher than an ideal value. An increase of the resistance in the ON-state and/or a decrease of the resistance in the OFF-state would be essential to fabricate a largely integrated AlO_x-ReRAM.

![Fig. 1](image)

Fig. 1 (a) Electric-pulse-induced resistance change measurement system. (b) The applied pulse pattern. The resistance is measured during the 'read' period. (c) Resistance vs. switching cycle number for anodic porous alumina.

3. Thermal properties

Conduction mechanism of the AAO memory cell has been investigated by measurements of the temperature dependence of the electric resistance and the thermally stimulated current. Electric resistance of an AAO memory cell in the ON and OFF state was measured between 2K and 300K cyclically. Figure 2a shows temperature dependence of resistance in the ON state. The resistance shows a linear decrease with decreasing temperature and a remnant resistance below 25 K. This is a typical metallic behaviour. Above 280 K, the resistance-temperature curve rises significantly in each heat cycle. The increase of the resistance with every heat cycle suggests a reduction of carrier numbers. Fig. 2b shows the temperature dependence of the resistance in the OFF state. The resistance decreases with increasing temperature and no hysteresis is observed after the temperature cycles. The OFF-state corresponds to an insulating or semiconducting state. We conclude that a metal-insulator transition is induced by the electric field.
The TSC measurement of AAO memory cell in the OFF state was performed from 79 K to 320 K with no bias voltage and heating rate of 0.15 K/sec. The measurement was repeated in six times. Figure 3 shows the TSC curves of the first and fifth cycle. TSC peaks are observed around 290 K with widths of 20 K in the 1st curve and 10 K in the 5th curve. The peak-intensity decreases with the number of heat cycles. The temperature of 290 K is close to the temperature where the anomalies of resistance in the ON state are observed. These suggest that the trapped carriers are released around 290 K. The appearance of TSC peaks indicates that localized states caused by the oxygen vacancy are located between conduction and valence bands. We can evaluate the trap level $E_i$ by using following approximation:

$$E_i = kT_m \ln(T_m^4 / \beta),$$

where $k$, $T_m$, and $\beta$ are Boltzmann constant, the peak temperature, and the heating rate, respectively [6, 7], and we estimated the localized level to be 0.6 eV. This result strongly suggests that the trapped carriers enhance the conductivity of anodic porous alumina.

4. Device on silicon substrate
In order to fabricate an integrated memory, we have developed an AAO memory cell on a SiO$_2$/Si substrate. Aluminum thin film of 1 µm in thickness was grown on a single crystal Si substrate covered with SiO$_2$ by electron beam evaporation technique. Then, the aluminum layer was anodized in 5 minutes and sintered in the acid for 2 minutes and anodized in 1 minute again. The condition of anodizing and removing oxide was the same as above. The measurement of the I-V characteristic was
carried out with an I-V analyzer at room temperature. Figure 4 shows that a clear resistance hysteresis was observed in this cell.

5. Conclusion
Transport properties of anodic porous alumina were investigated for $M/\text{AlO}_x/\text{Al}$ ($M =$ aluminum or silver) devices. The change of the electric resistance induced by electric pulse between the electrode and the aluminum substrate is huge and reproducible. The TSC measurement was carried out and the carrier trapped level was estimated to be 0.6 eV below the conduction band. Anodic porous alumina can also be operated on a SiO$_2$/Si substrate. Consequently, we believe anodic porous alumina is a promising material for a next-generation nonvolatile memory and other electrical applications. The AlO$_x$-ReRAM can be produced in simple process without poisonous or rare elements.

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