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Formation and disruption of current paths of anodic porous alumina films by conducting atomic force microscopy

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Anodic porous alumina (APA) films have a honeycomb cell structure of pores and a voltage-induced bi-stable switching effect. We have applied conducting atomic force microscopy (CAFM) as a method to form and to disrupt current paths in the APA films. A bi-polar switching operation was confirmed. We have firstly observed terminals of current paths as spots or areas typically on the center of the triangle formed by three pores. In addition, though a part of the current path showed repetitive switching, most of them were not observed again at the same position after one cycle of switching operations in the present experiments. This suggests that a part of alumina structure and/or composition along the current paths is modified during the switching operations.

Keywords: Anodic porous alumina, Scanning probe microscope, Conducting atomic force microscope, Resistive RAM, Current path

1. Introduction

Resistive random access memory (ReRAM) using a voltage-induced bi-stable switching effect of various metal-oxides and perovskites has been studied in recent years [1-4], because this is regarded as a potential candidate for the next-generation non-volatile memory. However, most of the proposed switching mechanisms depend on the materials and understanding of the mechanisms is still not enough. This is one of the main reasons why ReRAM is not made for practical use until now.

As concerns the switching mechanism, filament models [1-3] are considered as a key for some of the ReRAM materials. Direct observation of the filaments is not easy, but there are some reports which observed them successfully in some of the materials such as $SrTiO_3$ [4,5] and NiO [6,7] by conducting atomic force microscopy (CAFM). CAFM is a powerful technique to observe surface morphology and electrical current simultaneously. The observed current is limited in some areas or spots, and these are interpreted as the terminals of conducting filaments. The filaments which are generated by forming process or exists essentially in the switching materials are basically stable for both cases, and it is considered that they never move nor repeat creation and disruption.

By the way, form a view of future shortage of natural resources and environmental problems, we are thinking that we should study more about functional materials which composed of abundant elements for practical uses. This way of thinking is more and more important from now on. Because natural resources for most of atomic elements are quite limited and it is not easy to continue mining for long period of time. In addition, the compounds which consist of the abundant elements are mostly harmless. Regarding the amount of natural resources for each element near surface of the earth, Clarke number is one of the standards [8]. Aluminum oxide consists of Clark numbers of 7.56%(Al) and 49.5%(O). This is the second abundant binary combination next to silicon oxide.

As concerns the switching effect of aluminum oxide, it has been reported that anodic porous alumina (APA) thin films have a voltage-induced bi-stable switching [9-11], though its mechanism is not known similar to most of the other ReRAM candidate materials. Thus we have noticed and started to develop this material for ReRAM.

The APA thin film has a honeycomb cell structure of pores and consists of inner and outer layers [12] as schematically shown in Fig. 1. Nuclear magnetic resonance (NMR) measurements reveal that the inner and outer layers have different atomic structures, i.e., the inner layer has less 6-corrdinated Al and has more 4- and 5-corrdinated Al relative to the outer layer [13]. It is expected that existence of the honeycomb cell and the inner/outer layer structures may play some roles for formation of current paths.

In order to discuss the switching mechanism from a standpoint of the filament model, the authors tried to observe terminals of current paths directly by CAFM similar to the earlier work of the other ReRAM candidate materials. As a result, we have observed terminals of the filaments at a certain point of the APA film structure. Moreover, we have found formation and disruption of the filament during switching operations. This behavior of the filaments in APA is contrastive to those reported in the other ReRAM materials. We have visualized processes of such filament behavior. These are main results of the present study.

2. Experimental

The APA films were formed by a two-step replication method [14]. 1-mm thick pure Al plates (99.99%) were used as a substrate after chemical mechanical polishing (roughness <10nm) and electrical polishing in a solution of perchloric acid and ethanol. The anodizing of the Al was carried out in a 0.3M oxalic acid solution at 20℃ for 3h with a Pt cathode at a constant voltage of 40V. Then the anodic oxide layer was removed in a mixture of phosphoric acid (6wt.%) and chromic acid (1.8wt.%) at 60℃ for 1h. Then the Al specimen was anodized again for roughly 5, 16, 27, 38, 49 and 60s under the same conditions to the first anodizing step. As a result, thickness of roughly 16, 49, 82, 115, 147 and 180nm APA films were obtained and used for the present experiments.

CAFM was measured by a use of Seiko Instruments Inc. SPI3800N/SPA300HV in contact mode with conductive tips. The tips with spring constant of 1.5N/m were made by Si coated with Rh or Au. Typical radius of the tips was 30nm. The tips were grounded through a current meter and a voltage (from -10V to +10V) was applied to the Al substrate during the measurements as shown in Fig. 1. Typical scan area was 500nm square, scanning rate was set from 0.2 to 1Hz for x-direction, and sampling points of x and y directions are 512 and 256, respectively. The applied force between conductive tip and the surface was about 1.5nN. The detection range of the current of the CAFM was from 0.01nA to 100nA. A surface image and a current image were obtained simultaneously. The measurements were done in pure Ar atmosphere or in the air. The experimental procedure of the switching operations and their confirmations is as follows:

(i) a small negative voltage is applied (typically -0.4V) to confirm that there are no current paths initially,

(ii) a negative voltage (typically from -2 to -10V) is applied to change the electrical state from OFF to ON,

(iii) the small negative voltage is applied again to observe terminals of current paths on the alumina surface,

(iv) a positive voltage (more than +0.4V) is applied to change the state from ON to OFF,

(v) the small negative voltage is applied again to confirm disappearance of the current paths,

(vi) repeating the procedure from (ii) to (v).

Relationship between the procedure from (i) to (v) and ideal I-V characteristic are schematically shown in Fig. 2. Real I-V characteristics showing the switching effect by CAFM were not obtained in the present work because of drift of the AFM scanner. A typical I-V curve of a memory cell for this material forming a top Al electrode is shown in Refs. [11,15] (note that the direction of applied voltage for these references are opposite.).

3. Results and discussion

First of all, the experimental conditions are as follows; the APA film thickness: 49nm, the coating of CAFM tips: Rh, and the scanning speed: 1Hz. Before applying voltages, a place whose cells have no structural defects in an area more than 500nm^2 was chosen by a wider scan. We have confirmed that there were no current paths in the area initially by the procedure (i). Figs. 3(a)-(c) show CAFM images obtained from the procedure (ii). The applied voltage was -2.75V. Fig. 3(a) is a surface image, and Fig. 3(b) is a current image. Fig. 3(c) is a synthesized image from Figs. 3(a) and (b). The electrical current was detected more than 20 places and the maximum current was about -2.6nA. Fig. 3(d) shows the synthesized image (similar to Fig. 3(c)) obtained from the procedure (iii) at the applied voltage of -0.4V. Since the piezoelectric scanning system has drift with increasing time, α is marked on a certain vertex of cell as a guide. Positions of the current detected are corresponding to those in Fig. 3(c), but the size of the areas became small and their number decreased relative to that of Fig. 3(c). In other words, only a part of the areas observed in the procedure (ii) formed smaller areas in (iii). Moreover, the positions of the current paths in the procedure (iii) were on the vertexes of cells.

These results indicate that the current paths of the APA film were localized, and the observed current spots or areas in the procedure (iii) are considered to be terminals of the filaments. As concerns why most of the current paths were formed around the cell boundaries especially on the vertexes, probable two factors are considered to be its origin. One is that shape of the Al substrate under the cell boundary is like a ridge and in particular the shape under the vertex is like a tip as depicted in Fig. 1, thus it is expected that the applied electric field concentrates around these points. The other is that the breakdown of the inner layer plays an important role for completion of the filaments, i.e., the inner layer may have a smaller resistivity or breakdown voltage relative to the outer layer, in other words, the filaments penetrate into the outer layer from the inner layer. As regards disappearance of a part of current paths from Fig. 3(c) to Fig. 3(d), the areas relatively smaller and lower current disappeared. This is probably due to the lower limitation of the detecting current.

On the other hand, currents were under the detection limit of 0.01nA during the procedure (iv) with an applied voltage of +0.4V. The procedure (iv) corresponds to the operation from ON to OFF state, and this is confirmed by the procedure (v). Noticeable change was not observed on the surface morphology after one cycle of the switching operation. To confirm the repetitive switching of the APA film, -2.75V is applied again as a second cycle of the procedure (ii). However, most of the observed current was less than -0.05nA and the number of places where the current was detected decreased to 1/2 (about 10 places) relative to the first cycle (shown in Fig. 3(c)), and the only 4-5 places corresponded to those in Figs. 3(c) and (d). The detected current was too small to check filament formation by the procedure (iii). Therefore, the applied voltage was changed to -3.0V for the second cycle of the procedure (ii). The maximum current observed was increased to more than 1nA and a few of new current paths were generated. Fig. 3(e) shows the synthesized image from the second cycle of the procedure (iii). Notations of A, B and C are corresponding to those in Fig. 3(d). It is noted that there were only three same places where the current was detected for both the first and second cycle though about 17 point was detected at the first cycle. In addition, only two of new places were added. Similar tendency was also observed at the third cycle of the procedure (iii). Only two places were common from the first through the third cycles. With increasing the switching cycles, i.e., increasing the absolute value of the applied voltage for the procedure (ii), the detected currents for each current path increased, then those for the procedure (iii) also increased and there was a tendency that their area increased. In addition, the voltage necessary for the procedure (iv) also increased. These situations have made difficulties of continuing the repetitive switching operation, because the conductive tip of the cantilever was frequently broken by currents above 100nA.

These results indicate that threshold voltages of the formation of filaments depend on the places. This is probably due to slight differences of the structures around each triple point especially for the tips of Al substrates. In addition, most of the formed filaments were ruptured after only one cycle of the switching operation. This suggests that the local atomic structures or compositions along the filaments changes after the switching operation. The APA film consists of amorphous structures and has the inner and outer layers [12] whose atomic structures are different [13]. In general, amorphous structure is thermally unstable. It is expected that the currents along the filaments generate heat and a local temperature rise occurs, then the atomic structures of these regions possibly change depending on their current densities and the thermal conductivity of the material. For example, it is speculated that a phase transformation from an amorphous Al_2O_3 to the most stable α-Al_2O_3 or to some other more stable phases such as another semi-equilibrium states of amorphous Al_2O_3 or metastable crystal phases is possible. This phase transformation may cause rupture of a part of the filaments. However, few current was observed for both the first and second cycles of the procedure (iv). Regarding the composition, Yoshida et al. have reported oxygen movement during resistance switching in NiO films [16]. They have found strong influence of oxygen in the atmosphere during CAFM measurements and have concluded that the oxygen moves to the anode side, and have suggested that the resistance change is caused by compositional change of the NiO surface. From the view of the oxygen influence, we have tried the CAFM measurements in the air instead of Ar gas atmosphere. However, the experimental results showed no fundamental difference between these two atmospheres. This means that the atmospheric oxygen does not affect the switching effect in the APA thin films.

From viewpoints of application, one might think that the APA film inherently includes disadvantage for ReRAM due to the following two reasons; the observed typical terminals of current paths were on the vertexes of the cells thus integration limit of the APA memory is restricted by the inter-pore distance of 100nm in the present case, and most of the current paths were not generated again after one cycle of the switching operation. However, these two problems will be solved as follows. The inter-pore distance is controllable at least in a range from 50 to 420nm [17], though the lower limit is not known. In addition, a part of the current paths is stable after the repetitive switching. If the differences between the stable and the unstable paths are disclosed and if these are controllable, high density ReRAM cells will be manufactured comparable to honeycomb cell density of the APA films. On the other hand, there are some fundamental differences between the present experiments and the actual devices, i.e., (1) typical thickness of the APA film for the devices is about 180nm, (2) Al or Ag is used for the top electrode materials of the devices, and (3) contact area of the top electrode (Rh tip) is limited to an atomic size and this small electrode is moving on the surface with a constant speed. As concerns (1), we have confirmed formation of the current paths for 16, 49 and 82nm thick films, but the current was under the detection limit for the films of 115, 147 and 180nm. We have measured CAFM for the 180-nm thick APA film with applied voltage up to ±100V connecting an external power supply. Although currents were detected less than -70V, the conductive tip have got damaged because of its much heavier currents relative to the above experiments. Thus this evaluation was failed. As regards (2), Au coated tips were used for the measurements, but there were no significant differences, though repetitive switching has reported by a use of Au thin film as a top electrode [10]. This is probably due to a part of current paths which show the repetitive switching effect and/or generation of new paths. As concerns (3), scanning speed was changed to 0.2Hz in the procedure (ii), however the results were basically similar to those for scanning speed of 1Hz, though there was a tendency that the size of observed terminals of current paths became somewhat larger.

4. Conclusion

In summary, the terminals of current paths which are considered as filaments have been observed around the vertexes of cells in the APA thin films by the CAFM measurements. A bi-polar switching operation is confirmed. A part of paths was repeatedly formed during several cycles of the switching operation, but most of them were disrupted after one cycle. New paths at different vertexes of cells were formed when the absolute value of the applied voltage is elevated. Modification of a part of alumina structure and/or composition along the current paths is suggested.

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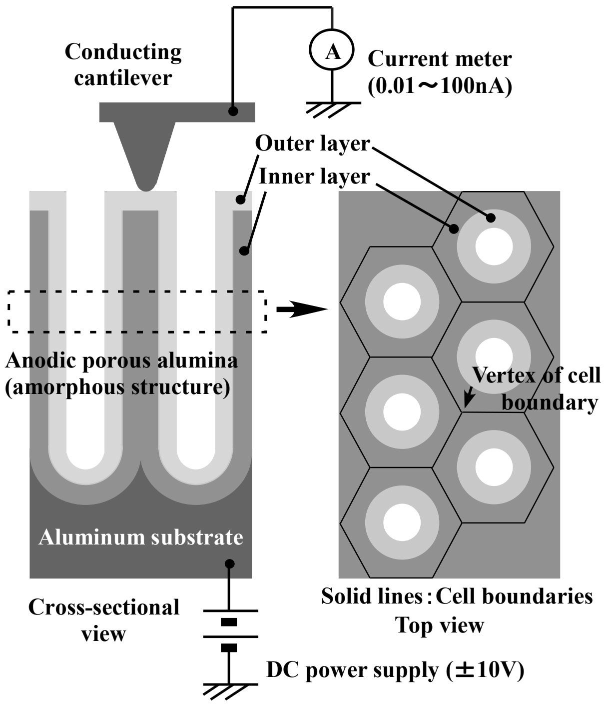

Fig. 1. Schematic diagram of APA film structure.

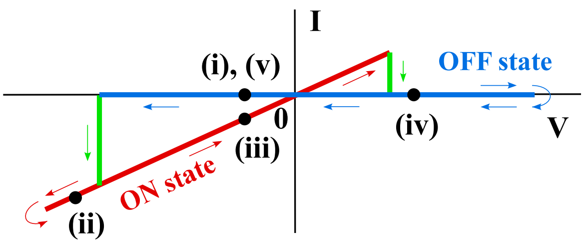

Fig. 2. Schematic diagram of ideal I-V characteristic which shows the memory effect and CAFM measurement points of the procedure from (i) to (v).

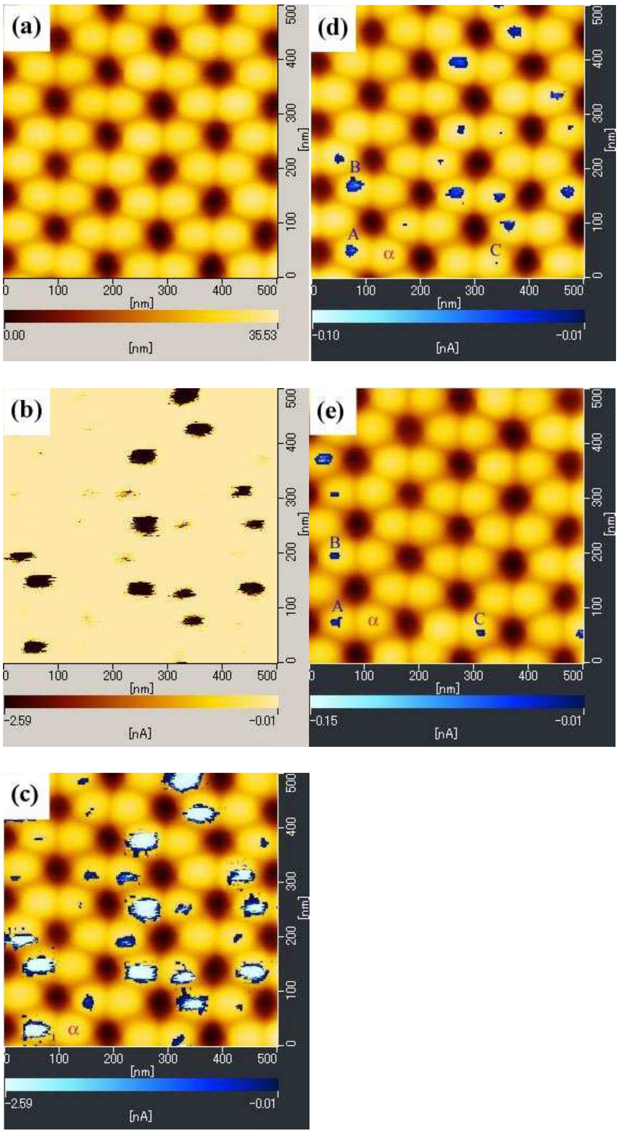

Fig.3. Simultaneously obtained CAFM images (a) surface image, (b)current image, and (c)synthesized image from both (a) and (b) at the first cycle of the procedure (ii), (d) synthesized image at the first cycle of the procedure (iii), (e) synthesized image at the second cycle of the procedure (iii).