The observation of “conduction spot” on NiO resistance RAM

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Abstract

We succeeded to observe the “conduction spot” (CS) in the capacitor structure ReRAM, which includes a conductive filament. In this study, we used NiO prepared by thermal oxidation at high temperature as 800°C. It requires a forming process by extra high voltage, which partly removes the top electrode from the resistance switched area. These experiments enabled us to observe the conductive filament directly in CS on NiO ReRAM by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From SEM images, CSs seem to be produced by some kind of breakdown, but we confirmed the reproducible resistance switching at least 50 cycles after the CS generation. By means of energy dispersive X-ray spectroscopy (EDX) with TEM observations, drastic oxygen reduction was recognized in local area within CS of NiO films. Moreover, the CS area depended on the injection power for forming. These experimental data suggest that miniaturization of ReRAM will be achieved by reducing the injection power for forming.

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1. Introduction

Resistance switching random access memory (ReRAM) has attracted much attention for the next generation memory because of its potential for high density, fast response, low power consumption, and nonvolatility on simple Metal/Oxide/Metal (MOM) structure.\(^1,2\) Many kinds of transition metal oxides have been reported as ReRAM materials, such as NiO, TiO\(_2\), CoO, CuO, etc.\(^3-11\) NiO is one of the most frequently reported materials with high on/off resistance ratio as a unipolar ReRAM device.\(^12-14\)

The unipolar resistance switching (RS) is widely believed to be caused by the formation and rupture of conductive filaments between top and bottom electrodes. Usually, the initial state of NiO thin films is the high resistance state (HRS). The forming process is needed to construct the filament, which is achieved by applying high voltage (\(V_f\)) to the MOM structure with appropriate current limitation. Then, the film is converted into the low resistance state (LRS). Afterwards, voltage \(V_r\) (\(< V_f\)) is applied to the film in LRS with no current limitation, and the state changes to HRS. It is called the RESET process. Finally, HRS is back to LRS by applying voltage \(V_s\) (\(V_r < V_s < V_f\)) with current limitation. This is the SET process. The reproducible RS is achieved by repeating SET and RESET processes. Although the RS phenomena and their reproducibility were reported and there are many analogical reasoning of reversible RS in metal oxides\(^2,9,11,12,14-24\), their switching mechanism has not yet been clarified. To reveal the RS mechanism, direct observations of conducting filaments are required.

In this study, we have conducted experiments focused on the forming process because this is a key to understand the RS mechanism and to control the switching property. It is believed that a thin filament is formed at very narrow area under the top electrode\(^2\).
This makes it difficult to identify the filament position. Hence, we carried out visualization of the position of filament formation. At first, we investigated the forming voltage of NiO films as a function of the oxidation temperature. It was revealed that NiO films prepared at high temperature around 800°C needs high electric power for forming. This high power injection for forming enables us to find out the position of the filament as a small conduction spot (CS). Afterwards, we observed CSs in NiO ReRAMs in detail by means of \textit{in-situ} optical microscopy (OM), scanning electron microscopy (SEM) as well as transmission electron microscopy (TEM). Conductive atomic force microscopy (C-AFM) and energy dispersive X-ray spectroscopy (EDX) were employed to analyze the conductive filament. As a conclusion, we showed that the size of CS which may relate to ReRAM scaling law is controllable by electric power injected during the forming process.

2. Experiment

Fabricated ReRAM devices have a simple MOM structure formed on a thermally oxidized Si (100) wafer such as Pt/NiO/Pt/Ti/SiO$_2$/Si as shown in Fig. 1(a). All films constituting the devices were prepared by radio frequency (RF) sputtering at room temperature. First of all, we deposited a 100-nm-thick Pt film as a bottom electrode (BE) with a thin Ti adhesion layer. Then, a 100-nm-thick Ni film was deposited on the BE. NiO thin films were formed by thermal oxidation in air at 500-800°C for 3 minutes. After chemical analyses of the oxidized Ni films by means of Ni-2p XPS (X-ray photoelectron spectroscopy), formation of NiO was confirmed$^{25}$). From XPS depth profiles, the films were fully oxidized at higher than 600°C (Fig. 1(b)) as reported in
earlier works\textsuperscript{26-27}, while the sample prepared at 500°C was oxidized only near the surface.

Finally, 50-nm-thick Pt top electrodes (TE) were deposited using a shadow mask. The size of TE was varied from 50 x 50 $\mu$m$^2$ to 1 x 1 mm$^2$. The electrical measurements of NiO ReRAMs were carried out at room temperature in air. An example of measured I-V characteristics is shown in Fig. 2(a). Typical curves of the unipolar ReRAM are recognized. The current in the forming and the SET processes was limited by the use of compliance of the measurement system (Yokogawa GS610). As widely known, the current compliance sometimes does not suppress the current overshoot due to fast switching speed of ReRAM and stray capacitance of the measurement system.\textsuperscript{5} Hence, we attached a resistor to a ReRAM cell in series for proper control of current limitation. The current overshoot must be much reduced while the influence by stray capacitance still remained. The injection power reached maximum just after the forming as shown in Fig. 2(b).

3. Results and Discussion

We first investigated the effect of oxidation temperature on ReRAM characteristics. In Fig. 3(a), the electrode area dependence of initial resistance (HRS) is summarized for fully oxidized samples, i.e. other than those at 500°C. The resistance was almost inversely proportional to the device area and increased by temperature. Therefore, there were no fatal film imperfections such as pin-holes. Figure 3(b) shows the dependence of forming voltage on the oxidation temperature, where the data of various TE sizes are superposed. By increasing the TE size, forming voltage tended to be low. The samples
oxidized at 500°C showed low forming voltage less than 2 V which is close to the SET voltages. This will be advantageous to practical use. As described above, these samples were oxidized only near the film surface, and the NiO layer was thin. Therefore, the voltage effectively works on NiO. In addition, the NiO layer must contain many weak spots (WSs) against electric voltage, such as oxygen deficient defects, grain boundaries, local modulation of the layer thickness, etc. This is thought to be another possible reason of low forming voltage. The forming voltage tended to increase at higher oxidation temperature, and it was widely distributed when we measured many devices (Fig. 3(b)). At the same time, the films became more resistive at higher oxidation temperature, while the whole films were oxidized in all cases in Fig.3(a). This means that the overall insulating quality of the NiO film was improved by high temperature annealing.

Samples oxidized at low temperature may contain many WSs with variety of threshold voltages ($V_{th}$) at which the insulating nature is broken. As a rough discussion, we assume a TE containing three WSs with $V_{th} = 2, 4$ and 6 V. In this case, the forming phenomenon occurs at the lowest voltage, i.e. 2 V. When the number of WSs is huge, almost all TEs contain at least one weakest WS and show forming at 2 V. Therefore, the distribution of the forming voltage is narrow. By increasing the temperature, part of the weakest WSs change to have medium $V_{th}$ (i.e. 4 V) or the strongest $V_{th}$ (i.e. 6 V). In this case, some TEs contain only WSs with $V_{th} = 4$ and 6 V while some of them are with all types of WSs. The forming voltage ($V_f$) of the former TEs is 4 V, while the latter TEs show $V_f$ of 2 V. The distribution of $V_f$ becomes wide. Since the probability to contain the weakest WSs is high for large TEs, $V_f$ tends to be lowered by the increment of TE size. In the present experiment, the oxidation time was only 3 minutes, and the NiO
films must be in this oxidation stage. Further oxidation may completely convert the weakest WSs to stronger ones, and the distribution width may be reduced. In this case, the forming voltage must be too high, and the films may not be used as ReRAM.

Summarizing these results and discussion, it is indicated that forming occurs preferentially on the weakest point of oxide films, which is the filament generation site. The forming process may have a relationship with the breakdown phenomenon as shown in the typical oxide films like a SiO$_2$ gate oxide. If forming is a process correlated to breakdown, the physical condition of NiO films after forming must be affected by injection power of forming. We adopted the NiO films formed at high oxidation temperature of 800°C on purpose to increase the forming voltage or forming power. By using this condition with high injection power, we successfully achieved to make the evidence of forming visible by means of OM (Fig. 4). There was nothing seen in the OM image on a TE before forming (Fig. 4(a)). At the moment of forming, in which RS from HRS to LRS occurred at the voltage of 5.6 V, an evidence (a small black spot in the OM image) was appeared on the TE (Fig. 4(b)). We call this forming evidence “Conduction Spot” (CS).

In order to confirm that the CS actually corresponds to the current path (filament) formation, we physically cut a device (500-μm-square) after forming at 5.3 V into two pieces as reported earlier\textsuperscript{14}). They are parts A and B in Fig. 5. It was confirmed that the part A with CS (circle 1) was kept in LRS of 60 Ω and the part B having no CS was in HRS (initial state) of 2.6 M Ω. Then, we performed a forming operation to the part B. A new CS appeared by the forming voltage of 6.0 V on the top electrode as shown in circle 2, and the resistance was changed to LRS of 108 Ω. In this figure, SEM images inside circles 1 and 2 are also presented. Crater like CSs in which the Pt TE has
automatically been removed are seen. Compared with the enlarged OM images, it is recognized that the CS size reflects the contrast of OM images. Moreover, we cut again the part B into parts C and D. Similarly, the part D was in HRS (initial state) of 3.8 M Ω, in which the resistance increased due to the reduction of the area. When the forming operation of 6.3 V was performed to the part D, a new CS appeared in the circle 3 and the resistance was changed to LRS of 49 Ω. These results strongly suggest that the CS corresponds to LRS. Forming voltage increased step by step with the order of forming step as shown in Fig. 6. This result supports the idea that the weakest WS in the oxide film was selected at each forming process and was a seed of filament formation. To check that the CS is not a point of permanent breakdown, reproducibility of RS after CS generation was investigated. As shown in Fig. 7, RS between stable LRS and HRS over the 50 cycles was achieved when we repeated SET and RESET operations.

To reveal that the CS is the position of RS switching, the details of CS was investigated by means of SEM (Figs. 8(a) and 8(b)) and C-AFM (Fig. 8(c)). Figure 8(a) is a SEM image showing a CS just after forming. Though the central part of the CS do not contribute to succeeding RESET-SET switch because Pt TE at this area has been automatically removed during the forming operation, they give us an important information. At this part, low resistance area was clearly confirmed as shown in Fig. 8(c). It is thought to be composed of wreckages of conductive path generated and broken by a violent forming operation. The individual area is very small on the order of 10 nm. If the forming with low power using the NiO film oxidized at lower temperature, the conductive area may be reduced to this size without any removal of the TE. In this case, however, it is hard to be observed by OM, SEM and C-AFM. After succeeding several SET-RESET operations as shown in Fig. 8(b), CS area protruded at the edge to
the lower direction of the image in comparison with Fig. 8(a). Correspondingly, low resistance area appeared here as indicated by an arrow, which was invisible under the TE just after the forming process. While this low resistance area no more contributes to further switching because the TE at this area has been already removed, this protrusion is understood to be formed by the power injected through this low resistance area. In other words, this protrusion may be caused by the extra SET-RESET operation, and the resistance change is thought to occur at the edge of CS.

From these results, the mechanism to generate the CS is considered as follows (Fig. 9). At the 1st stage of forming, a conductive filament appears at a CS by the application of voltage (Fig. 9(a)). By current flow through the filament, Joule heat is generated and diffuses to the neighboring region. This region becomes weak against voltage after agitation by heat, and many filaments are generated around the 1st filament as shown in Fig. 9(b). Finally, heat generated by these plural filaments melts NiO in the CS area and explosion occurs. Only at the edge of the CS, filaments barely keep connection between TE and BE and contribute to succeeding RS (Fig. 9(c)). Though this forming is quite violent, the filaments remaining at the edge of the CS are thought to act as filament produced at lower voltage with proper current limitation. In this work, the high power forming was performed in order to detect the position of the area containing conductive filaments, and the CS was detected. By low power forming and succeeding RS, ReRAM phenomenon is expected with less number of conductive filaments without the formation of a crater. Further direct observation should be needed to reveal the filament formation mechanisms more clearly by the use of in-situ TEM.28-29)

As described above, the conductive filament was expected to be formed at the CS edge. To investigate the CS in detail, cross sectional TEM observations with EDX
analyses were carried out (Fig. 10). A sample containing a CS was cut along arrow heads in Fig. 10(a). The corresponding TEM image and an enlarged one at an edge of CS are shown in Figs. 10(b) and 10(c), respectively. NiO was thought to be melted by forming, and recrystallized. The Pt TE was aggregated to the edge from the interior of the CS, and a half of NiO films were moved to the exterior of the CS. Although these images suggest some kind of breakdown occurred, it was not a permanent one because reproducible RS was observed. As discussed above, conductive paths (filaments) are thought to be at the edge of CS. We analyzed the CS edge to figure out the composition of NiO by EDX as shown in Fig. 10(c). The chemical compositions in the CS are roughly classified into three groups, while it was Ni:O ≈ 1:1 out of CS (for example, at the left end of the NiO film in Fig. 10(b)). The triangles slightly far from this edge showed the composition of Ni:O ≈ 1:1. On the other hand, the compositions of the region indicated by circles and squares at the edge were Ni:O ≈ 9:1 and 2:1 respectively, indicating the existence of oxygen deficient NiO. This area may play as the filament path giving the RS phenomenon. Since this TEM image was taken after RESET process, the filament path should be discontinuous although no clear evidence was not given in this observation.

When we scale down the size of ReRAM for large scale memory applications, structural change of NiO thin films must be miniaturized. Figure 11 shows the SEM images of CS formed with various resistors for comparison. Since the forming voltage of the samples oxidized at 800°C widely dispersed as shown in Fig. 3(b), the perfect control of CS size by resistors was not realized. We can describe only roughly that the large series resistor tended to reduce the CS size. On the other hand, the CS size has a clear relation with the injected power at the forming process. Here, it should be noted
that the injection power does not mean the total power for the formation of CS, but the maximum power injected during the forming process (maximum value of voltage × current until the current reached to the value for limitation). As seen in Fig. 12(a), a hole was sometimes formed under TE. It cannot be recognized from SEM images. Therefore, in this report, the area including the bank of the CS (dotted curves in Fig. 12(b)) was used as the CS area in order to prevent underestimation of the size. In Fig. 12(c), we plotted the CS area as a function of the injection power. Almost proportional relation between CS area and injection power was achieved. This result shows a great potential for scaling of RS. If we can extrapolate the relation to the nanometer scale, the CS size can be diminished to less than 10 nm by reducing the forming power of 10^{-7} W. This size is comparable with the size of wreckages shown in Fig. 8(c).

**Conclusion**

We succeeded to identify CS which is the platform of filamentary conduction in a NiO based ReRAM. The key point of the visualization of CS is the injection power control for forming process by setting the oxidation temperature as high as 800°C. Probably CS appears at a “weak spot” in the NiO film by forming. In this CS area, there is the conductive filament with high oxygen deficiency as analyzed by EDX measurements. The size of the low resistance area is on the order of 10 nm. Moreover, almost proportional relation between the CS area and the injection power was confirmed, which suggests great potential for scaling of NiO ReRAM. This relation is very preferable for miniaturization of large-scale integration of ReRAM.
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References

Figure Captions

Fig. 1 (a) Schematic drawing of the NiO MOM structure. (b) XPS depth profile of a NiO film oxidized at 600°C.

Fig. 2 (a) Typical DC $I$-$V$ characteristics with current compliance of a voltage source. The horizontal axis denotes the output voltage of the voltage source. (b) The $I$-$V$ characteristics (black curve) and the power (red curve) in the forming process with a series resistance of 100 kΩ. The horizontal axis denotes the voltage actually applied to the ReRAM device. At the moment of forming (ca. 7 V), this voltage suddenly decreased to about 0.2 V because of the abrupt reduction of the device resistance.

Fig. 3 (a) Initial resistance as a function of TE area for NiO films oxidized at 600 - 800°C. The resistance was evaluated at 1 V. (b) Forming voltage as a function of oxidation temperature.

Fig. 4 In-situ images (a) just before and (b) just after forming (current compliance of 2 mA), which show OM images of a 100-μm-square TE compared with simultaneously measured I-V curves (right-bottom of each figure). The interval between (a) and (b) is 150 ms. Forming voltage was 5.6 V. CS (black dot) appeared near the center of the TE at the moment of forming. The CS position is independent
on the position of the probe used for electric measurements.

**Fig. 5** OM images after repeating the processes of forming and cutting the device with a 500-μm-square TE. The part A is an area including the CS appeared during the 1st forming. The device was cut into two pieces such as A and B. It was confirmed that A is in LRS and B is in HRS. Then we performed the 2nd forming resulting that B included a CS. The part B was cut into C and D which were in LRS and HRS, respectively. Then we performed the 3rd forming to the part D giving a new CS. For clarity, enlarged OM images (x 5) and SEM images of CSs are inserted. Scale bars in SEM images denote 1 μm.

**Fig. 6** Forming voltage as a function of the order of the forming step: the 1st, 2nd and 3rd forming.

**Fig. 7** SET and RESET processes between LRS and HRS after observing CS. Reproducibility of resistive switching over 50 cycles was yielded after CS was formed.

**Fig. 8** (a) and (b) SEM images of CS before and after the repeating SET-RESET process in several times, respectively. CS was expanded by additional injection process. (c) Corresponding C-AFM image to (b). Many small multiple low resistance areas were detected in CS where the TE is removed. In the region with an arrow, additional low
resistance areas by RSs can be observed.

Fig. 9 Schematic drawings of CS formation.

Fig. 10 (a) SEM image, (b) and (c) corresponding TEM images of CS. In (c), the edge of CS is enlarged, where the conductive path (filament) is thought to be formed. Around this area, compositional analyses of NiO were performed by the use of EDX. The triangles, squares and circles correspond to positions with composition ratios of Ni:O = 1:1, 2:1, and 9:1, respectively.

Fig. 11 SEM image of CS area controlled by injection power with respective current compliance using serial resistors of (a) 10, (b) 20, (c) 100 and (d) 470 kΩ. The maximum injection power for each figure is (a) 2.3, (b) 2.8, (c) 0.50 and (d) 0.11 mW.

Fig. 12 (a) Cross-section TEM image showing the existence of a hole inside the film. (b) Corresponding SEM image. The area in the broken curve is the estimated CS area. (c) CS area as a function of maximum injection power. The slope of the red line is unity.
Fig. 1
Fig. 2
Fig. 3
Fig. 4

(a) dust
Pt TE
Pt-Ir probe
NiO

(b) dust
50 μm
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Joule heat

Initial filament at a weak spot

Plural filaments

Explosion

Fig. 9
Fig. 10
Fig. 12