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In-situ transmission electron microscopy of conductive filaments in NiO resistance random access memory and its analysis

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We used thermal oxidization at various temperatures to prepare NiO/Pr-Ir for use in resistance random access memory (ReRAM) samples. *In-situ* transmission electron microscopy (TEM) was used to investigate the forming process of these ReRAM samples, where a needle-shaped top electrode of Pt-Ir was attached to the NiO/Pt-Ir ReRAM layer. The forming voltage initializing the NiO layer increased at an oxidization temperature of between 200 and 400 °C. In this process, conductive bridges, which are thought to be conductive filaments of a ReRAM, appeared, and their sizes showed a correlation with the injection power. It was as small as about 300 nm^2 when the injection power was 10^{-6} W. Energy dispersive X-ray spectroscopy was used to analyze the bridge, and it was experimentally confirmed that the oxygen content of the bridge was lower than that of the initial NiO layer. However, these bridges in the low resistance state did not show further ReRAM switching to the high resistance state inside of a TEM instrument. To check the reason of this result, we investigated samples outside of the TEM instrument, which had similar geometry to that of TEM specimens. They showed the ReRAM switching in air ambient but not in vacuum. Combining these results inside and outside of the TEM instrument, it can be concluded that the existence of oxygen around the conductive filament plays an important role. This supports the filament redox model on the ReRAM operation.
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I. INTRODUCTION

Some metal oxide films, such as Pr-Ca-Mn-O (PCMO), NiO, CuO, TiO_2, CoO, are known to exhibit an enormous resistance change when voltage is applied to them. Investigations into developing a new type of nonvolatile memory called a resistance random access memory (ReRAM) are intensively conducted using this resistance switching.[1–9] The ReRAM has high functionalities such as high-speed access, high integration, low power consumption, and non-volatility. In addition, the fabrication method for producing ReRAMs is compatible to the CMOS process. The resistance switching of binary oxides such as NiO is mainly of the unipolar type that does not depend on the voltage polarity.[10–16] Recent works reported that the "filament-redox-model" (in short, the "filament model") is influential in unipolar resistance switching.[4,17–21] In the first process of this ReRAM operation, a relatively high voltage applied to the initial ReRAM film in the high resistance state (HRS, off-state) changes it to the low resistance state (LRS, on-state). This initializing operation is called "forming" and is carried out based on a current limitation (in other words, current compliance) to prevent permanent destruction of the device. Following the filament model, it is believed that conducting paths called filaments are formed inside the oxide layer and connect to the top and bottom electrodes (TE and BE, respectively) sandwiching the oxide layer. As a result, the resistance becomes low. After this process, voltage of the same polarity is applied to the device in the LRS by removing the current limitation. This is called the "reset" process. Running a high current through the filament causes it to rupture probably due to oxidization, and the resistance state then is in the HRS. Subsequent voltage application with current limitation changes the resistance to the LRS. This operation is called "set," where the conduction of the filament is recovered. The ReRAM function is thus achieved by repeating the reset and set operations.

Many reports anticipated that the conductive filaments contribute to the resistive switching not only in unipolar ReRAM materials but also in materials for bipolar operations where the alternation of the voltage polarity is required for switching.[3,4] Therefore, it is important to investigate the filaments to clarify the ReRAM switching mechanism. There have been some attempts to observe and analyze the filaments.[22–25] They were mainly *ex-situ* experiments after the resistive switching, and exploration of the tiny filaments seems hard because the filament formation occurs randomly in the device area.[24] More direct information about the filaments can be accumulated by dynamically observing the switching processes. One method is *in-situ* transmission electron microscopy (TEM), where electric measurements and geometric and crystallographic observations can be simultaneously performed.[26–29] Three types of materials

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have been investigated by *in-situ* TEM. The first one was PCMO which shows the bipolar switching.[30–32] By applying the voltage with resistance change, structural change probably caused by oxygen migration was reported at the vicinity of the interface between the electrode and PCMO.[30,32] Importance of the electronic state around the interface was pointed out. The second one was solid electrolytes with Cu or Ag electrode.[33–37] During the set and reset operation, the formation of metallic filament composed of Cu or Ag connecting electrodes and its rupture were experimentally proved. In these two kinds of materials, the forming process is not required in general cases. On the other hand, binary oxides showing the unipolar as well as bipolar switching generally need the forming process while the ReRAM device with very thin oxide layer occasionally does not need this process.[38,39] The devices are easily eternally broken during the forming process where a high level of electricity is used, and the *in-situ* TEM observation is thought to be hard as pointed out by Schroeder *et al*.[40] In a work on Ti-O by Kwon *et al*.,[41] they observed a phase transformation in a filament during the set and reset operation. It was pointed out this phase transformation between the conductive Magneli phase and other insulating phase contributes to the ReRAM switching. However, their work was on the sample after the forming process. By using a serial resistor in the measurement circuit to suppress current overshoot during the forming process,[8,40] Fujii *et al.* performed a real-time observation of the forming process of NiO.[42] A tiny conductive region called the "bridge" was formed during the abrupt decrease in resistance. The bridge region had a much lower level of resistance than those of the adjacent regions, and the bridge was clarified to contain the conductive filament contributing to the ReRAM switching. However, the details of the resultant filaments, such as size, composition, as well as the ReRAM switching property, are not yet systematically investigated.

As described above, the conductive filament is expected to play a key role in the ReRAM switching, and thus, controlling the bridge formation in the forming process is important. In this work, therefore, we investigated the bridge size using various injected electrical power levels by means of *in-situ* TEM on NiO thin films. The obtained conductive bridge was analyzed by using energy dispersive X-ray spectroscopy (EDX), and it was clarified the bridge contained less oxygen than the NiO pristine layer. However, further reset and set operation was not realized in TEM. In order to investigate the influence by the vacuum ambient, the ReRAM switching of NiO using a tip-shaped top electrode was measured outside of the TEM instrument. The reset operation after the forming process was not realized in a vacuum while it was recognized in air. Oxygen is thought to play an important role in the resistance switching of unipolar NiO ReRAMs.

II. EXPERIMENTAL PROCEDURE

In the first step of sample preparation, a 25-nm-thick Ni (99.99%) thin film was deposited (RF-sputtering, 100 W) on a wedge-shaped Pt-Ir substrate prepared by using the ion-milling method. The substrate works as the BE. Afterwards, it was thermally oxidized at 200–800 °C for 3 min (environmental humidity of about 30%). The obtained NiO film was about 40 to 50-nm polycrystalline. The NiO grain size was about 30–50 nm. This oxidization condition may provide sufficient resistance switching properties as proved in Pt/NiO/Pt patterned devices (100-nm-thick and oxidized at 500–800 °C) on SiO_2/Si wafers.[16,24]

The *in-situ* TEM observation system was composed of a custom-made TEM holder attached with a piezo actuator.[26–29] The TEM instrument we used was mainly a JEM-2010 microscope (200 kV, $C_s = 0.5$ mm, 10^{-5} Pa) with a CCD video camera to record the TEM images. In the TEM holder, the wedge-shaped ReRAM sample described above and a tip-shaped counter electrode made of Pr-Ir working as a TE were placed. The ReRAM sample was fixed and electrically grounded while the TE was movable and electrically biased. The typical apex size of the TE was 20–40 nm, which is comparable to the NiO grain size. The conduction properties were measured by touching the TE to the NiO/Pt-Ir. The best location for measuring the current-to-voltage (I-V) characteristics was selected on the fixed NiO/Pt-Ir sample by moving the Pt-Ir TE. The electrical measurements were performed by using a Yokogawa GS610 source measure unit (SMU) at room temperature. The details for the experimental setup can be seen in Refs. 36 and 42. Because of the lack of an EDX facility, the sample after forming was quickly transferred to another microscope (JEM-2010F), and its oxygen content was analyzed by using EDX. The electron beam size for the EDX was typically less than 10 nm in diameter. Although slight oxidization must occur during the transfer in air, we believe it did not induce a fatal problem in the conclusion.

In addition to the TEM samples, flat NiO films were formed on Pt/SiO_2/Si substrates to check the environmental influence. They were prepared by using thermal oxidation at 600 °C for 3 min after the RF sputtering deposition of 100-nm-thick metallic Ni. The ReRAM properties were measured by using the SMU described above in air and in a vacuum (about 10^{-3} Pa). Two types of TEs were tested. One was a probe for scanning tunneling microscopy (STM) made of Pt-Ir, which was in direct contact to the NiO layer. The contact size was typically several μm to 30 μm. This is an analogous geometry of the sample for *in-situ* TEM. The bridge generated in the forming process is exposed directly to air or to a vacuum. The other one was a patterned device in which sputter-deposited Pt was used as the TE (100-nm-thick, $100 \times 100\ \mu m^2$). In this case, the bridge was expected to be encapsulated in the ReRAM device.

III. RESULTS AND DISCUSSION

A typical I-V curve during the forming process is shown in Fig. 1(a), where a load resistor of 100 kΩ is serially connected with the ReRAM sample oxidized at 200 °C. By increasing the applied voltage to 2.75 V, the current abruptly increased approximately to the value for the load resistor. A typical TEM image just after forming is shown in Fig. 1(b). A small conductive bridge (about 32 nm wide) was formed around the TE probe attached to NiO. The resistance of the

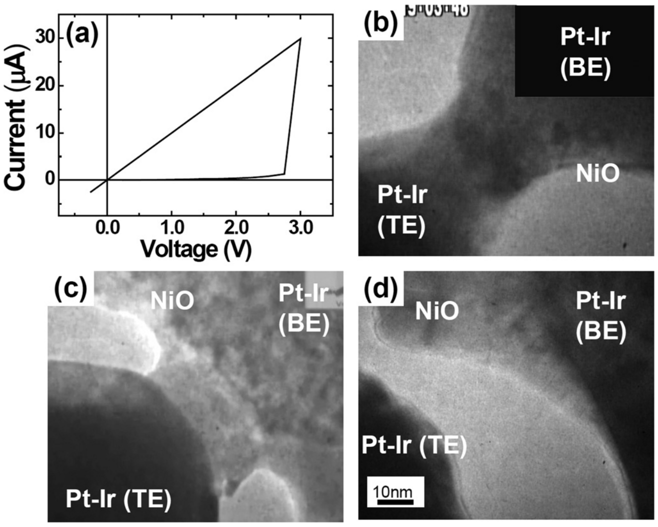

FIG. 1. (a) I-V curve at forming and (b) a typical TEM image (after forming) of NiO oxidized at 200 °C. (c) TEM image of samples oxidized at 300 °C after forming. Bridges appeared in the forming process, and the sizes were larger than the bridge shown in (a). (d) Sample oxidized at 500 °C after forming. The NiO film was destroyed by the high level of injection power.

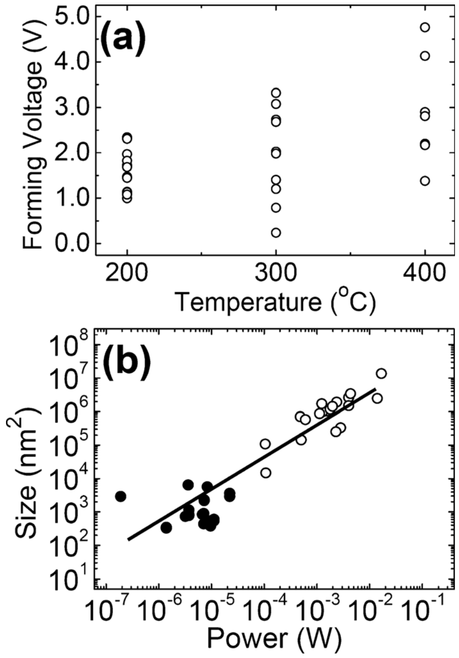

FIG. 2. (a) Forming voltage as function of oxidation temperature. (b) Bridge size (full circles) for various levels of injection power superposed on CS size by Kondo *et al.* (open circles).[24] The line is an extrapolation of open circles, on which the data for the bridges are gathered.

bridge was usually 50–100 Ω while the adjacent NiO layer maintained the initial value (ca. 2 MΩ). As reported earlier,[42] the bridge may work as a conductive filament contributing to the ReRAM switching.

A. Forming power and the bridge size

The forming voltage of the sample oxidized at 300 °C tended to increase and the bridge size was large as recognized in Fig. 1(c), where the bridge diameter was about 45 nm. This was also true for the sample oxidized at 400 °C. On the other hand, in the NiO samples oxidized at more than 500 °C, the sample was destroyed due to the high forming power, and no conductive bridge remained near the TE, as recognized in Fig. 1(d).

The forming voltage of the samples providing the bridges is summarized in Fig. 2(a). The samples oxidized at 200 °C had a low forming voltage. By increasing the oxidation temperature, the forming voltage tended to be high and its distribution widened. This phenomenon corresponds to the result from flat Pt/NiO/Pt devices prepared using thermal oxidation.[24] The degree of oxidation is expected to be with the increase in temperature. Therefore, the averaged forming voltage increased with the oxidation temperature. In addition, because the oxidation time was short at 3 min, the oxidation is thought to be inhomogeneous with weak spots against voltage application such as in the weakly oxidized region, grain boundary, and local modulation of the layer thickness. These weak spots may be the nuclei of the filaments. Compared with the sample at 200 °C, the number density of the weak spots must decrease for the high temperature oxidization at 300 and 400 °C. When the small TE probe hits a weak spot, the forming voltage is low. On the other hand, it must be high when the TE avoids it. This may be the reason for the voltage dispersion in Fig. 2(a). At a temperature higher than 400 °C, the overall insulating quality of the NiO film is thought to be greatly improved. In this case, too much electric power is required for initialization. Therefore, film destruction occurred, as shown in Fig. 1(d).

Many reports have claimed that the filaments are formed by a soft breakdown.[4,6,7] Even with the word "soft," the forming is a wild process for breaking the insulating property. Thus, controlling the forming power and the resulting bridge size are important factors for ReRAM switching. Kondo *et al.*[24] observed crater-shaped "conduction spots" (CS) during the forming process at the edges of which switchable filaments existed. They reported that the CS area was almost proportional to the injection power (they used the maximum value just before a resistance change). Relating to this report, the cross sections of the bridges were estimated from the TEM images by assuming the circular sections. The bridge sizes (i.e., cross sections) are summarized (full circles) as a function of the injection power and are plotted in Fig. 2(b). In this figure, the CS data by Kondo *et al.*[24] are superposed as open circles. The data points of the bridge sizes are on the extrapolation line of the CS size. Therefore, it is assumed that the bridges are small CS. The bridge size was ~300 nm^2 (corresponding to about 20 nm in diameter) at an injection power of 10^{-6} W, and the size is expected to be less than 100 nm^2 (~12 nm in diameter) when the forming power is about 10^{-7} W. This shows there is great potential for the scaling of resistive switching. Even in the present work using a serial resistor, current overshoot in the forming process cannot be completely eliminated because parasitic capacitance of the circuit in the *in-situ* TEM holder still remains. In real ReRAM devices where field effect transistors (FETs) are placed just near the switching layers, these size may be smaller.

In a previous literature, oxygen deficient area was experimentally recognized at the grain boundary.[22] The resistivity around the grain boundary is expected to be low, and this was experimentally confirmed by means of *in-situ* TEM.[42] Formation of conductive filaments and further ReRAM switching would preferentially occur around the grain boundaries.[11,43] Because of the less insulating property at the grain boundary, soft forming is expected, and possibility of permanent breakdown must be reduced.

B. Oxygen content of bridge

Following the filament model of binary oxides, the redox reaction of the conductive filaments contributes to the ReRAM switching.[4,8,19–21] In this section, the oxygen content of the bridge that appeared during forming will be discussed. Figure 3(a) shows a TEM image of the bridge region of the sample shown in Fig. 1(c) (oxidized at 300 °C), but after detaching the TE probe. The slightly darker region at the center of the image corresponds to the wreck of the bridge and the surrounding region is NiO in the initial state, while the dark contrast at the top of the image corresponds to the Pt-Ir BE. The square and circle symbols indicate the positions where the EDX analysis was performed. A typical EDX spectrum from the points with the squares (initial NiO region) is shown in Fig. 3(b). On the other hand, the points with the circles (bridge region) gave the spectrum from Fig. 3(c). Apparently, the oxygen peak was weakened in the bridge region. By assuming the thin foil approximation, the estimated composition of Ni:O was 71:29 for Fig. 3(b), while it was 85:15 for Fig. 3(c). Although this approximation provides a rough estimation to discuss in more detail, it is summarized by stating that the bridge region with a lower resistance contained a smaller amount of oxygen compared with the initial NiO layer. This result fits with the phenomenon expected in the filament model of binary oxides.

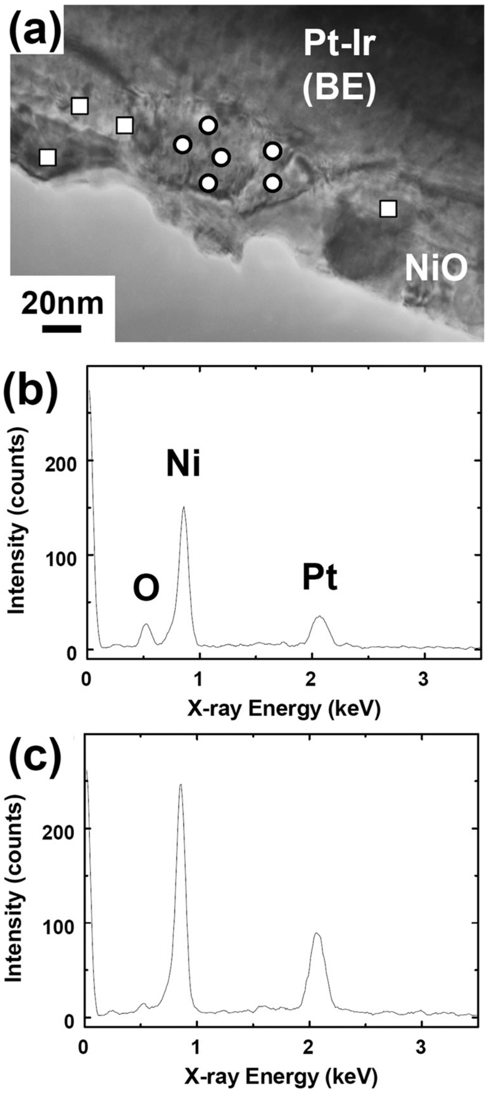

FIG. 3. (a) TEM image of bridge in NiO sample shown in Fig. 1(c) oxidized at 300 °C, after detaching tip-shaped TE. At the center of the image, there is a conductive bridge. The squares and circles denote the positions in the initial NiO and in the bridge regions where EDX analyses were performed, respectively. (b) and (c) Typical EDX spectra from initial NiO layer and from bridge region, respectively. The relative concentration was estimated to be Ni:O = 71:29 and 85:15 from (b) and (c), respectively.

C. Influence of oxygen in ReRAM switching

It was experimentally confirmed through TEM experiments that the injection power for forming controls the bridge size and that the conductive bridge contains less oxygen than the initial NiO. However, the reset operation was not found during the TEM observation. This may be due to the vacuum ambient inside the TEM instrument. In order to clarify this prediction, we prepared the NiO layer on Pt/SiO_2/Si substrate as described in the last part of Sec. II. A schematic drawing of the sample is shown in Fig. 4(a). The Pt-Ir TE was put into contact on the NiO surface to use similar geometry to the condition in the TEM. The measurements were carried out in air or in a vacuum, both of which were performed outside of TEM. Figure 4(b) is the typical I-V cycles measured in air after forming. The forming voltage was relatively large because of the thick NiO layer oxidized at 600 °C with a small contact area. However, a resistance switch with several tens of cycles was confirmed. On the other hand, after we evacuated until achieving about 10^{-3} Pa, the sample generally did not show a reset operation. In Fig. 4(c), an example is presented where the compliance value was gradually increased from A to D, but no resistance change was recognized up to a current of about 500 mA. In a vacuum ambient, the bridge cannot get oxygen from its surroundings. This supports the idea that the reset operation occurs based on the oxidation of the filaments.[17,20,21] The forming voltage of various positions selected by the tip-shaped TE is summarized in Fig. 4(d), where the horizontal axis denotes the measurement sequence corresponding to time. The circles are the data before the evacuation, the triangles are the data in a vacuum, and the squares are those after breaking the vacuum. The full symbols denote the data showing plural reset-set operations. The reset-set operations were generally recognized before the evacuation. The forming voltage gradually increased and the reset operation was not observed during the evacuation. After vacuum breakage, the voltage decreased and the reset-set operation was recovered, but such changes required some time interval. From this result, the water vapor in the air is also expected to influence the forming and reset-set operations of an open system

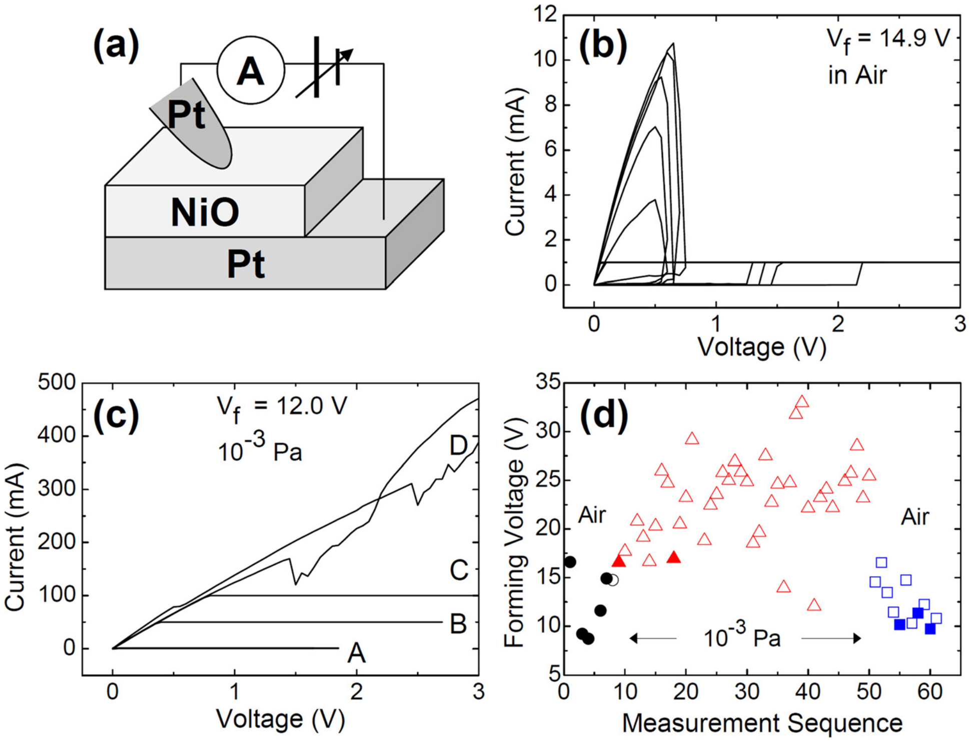

FIG. 4. (a) Schematic drawing of sample structure measured outside a TEM instrument, where tip-shaped TE was used. (b) and (c) Typical I-V curves after forming with voltage V_f in air and in vacuum, respectively. No reset operation was seen in (c) during the stepwise increase of the current compliance from A to D. (d) Forming voltage measured before evacuation (circles), in vacuum (triangles), and after breaking vacuum (squares). The data were obtained after selecting various points using the movable tip-shaped TE. The horizontal axis is the measurement sequence corresponding to time. Full symbols denote the data with plural reset-set switching after forming while the open symbols are the data without such switching. The environment influences the ReRAM property when the tip-shaped TE shown in (a) was used.

as shown in Fig. 4(a), where Pt/NiO interface is directly exposed to air or vacuum.

In contrast, the sample with a deposited TE (patterned device) provided a different result. The endurance property of this sample is presented in Fig. 5. The ReRAM switching with an on/off ratio of more than 100 was continuing even after the evacuation. In this case, the result can be understood as follows. The oxygen appeared due to the reduction in forming and the set operations were kept inside the device, and it was used for the oxidation of the filament in the reset process.[44]

Based on this hypothesis, the phenomenon appearing in the *in-situ* TEM observations will be discussed. The structural change of the NiO layer may explain the oxygen movement, as shown in Fig. 6. By applying a positive voltage to the TE, oxygen inside the initial NiO layer migrates along the direction from the BE to the TE (Fig. 6(a)). As a result, excessive and deficient oxygen regions appear under the TE, and some stress is generated. The injection power sometimes causes the NiO layer to melt.[15] Therefore, the dense oxygen around the probe-type TE diffuses into a vacuum (Fig. 6(b)). As a result, an oxygen deficient region and melted region remain in the NiO layer after forming (Fig. 6(c)). This may be the mechanism of the bridge formation in the TEM instrument. In this case, a well oxidized NiO region with the ability to supply oxygen does not remain around the bridge. Moreover, in the TEM instrument, the bridge is exposed to a vacuum without sufficient oxygen. The conductive filaments inside the bridge do not have a chance to be oxidized for the reset operation (Fig. 6(d)). In order to perform *in-situ* TEM observations of NiO or other binary oxides showing the unipolar ReRAM switching, additional experimental tricks will be required, e.g., experiments using a piezo-holder attached to an environmental TEM.

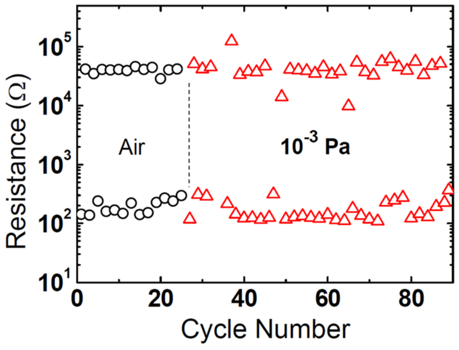

FIG. 5. Endurance property of Pt/NiO/Pt ReRAM with sputter-deposited TE instead of tip-shaped TE, where circles and triangles denote data obtained before evacuation and in vacuum, respectively. The reset-set switching was recognized both in air and in a vacuum. The current compliance of 1 or 2 mA was used in the set process. The resistance was evaluated just before the set or the reset changes occurred.

IV. SUMMARY AND CONCLUSION

The forming process of the NiO layer prepared by using thermal oxidization was studied by means of conducting an *in-situ* TEM to investigate the switching mechanism of unipolar ReRAMs. The forming voltage was large and its distribution widened when the sample was oxidized at a high temperature. This phenomenon may be caused by improving the insulating quality of NiO film. The bridge size showed a correlation with the forming power. The bridge diameter was about 20 nm when the forming power was about 10^{-6} W. With a well controlled NiO insulating layer, the forming power may be further reduced, and a ReRAM size of less than 20 nm is assumed to be possible. The obtained bridge was analyzed by using TEM-EDX, and it was confirmed that the bridge region showed a low level of oxygen concentration compared to the initial NiO. This supports the model that the

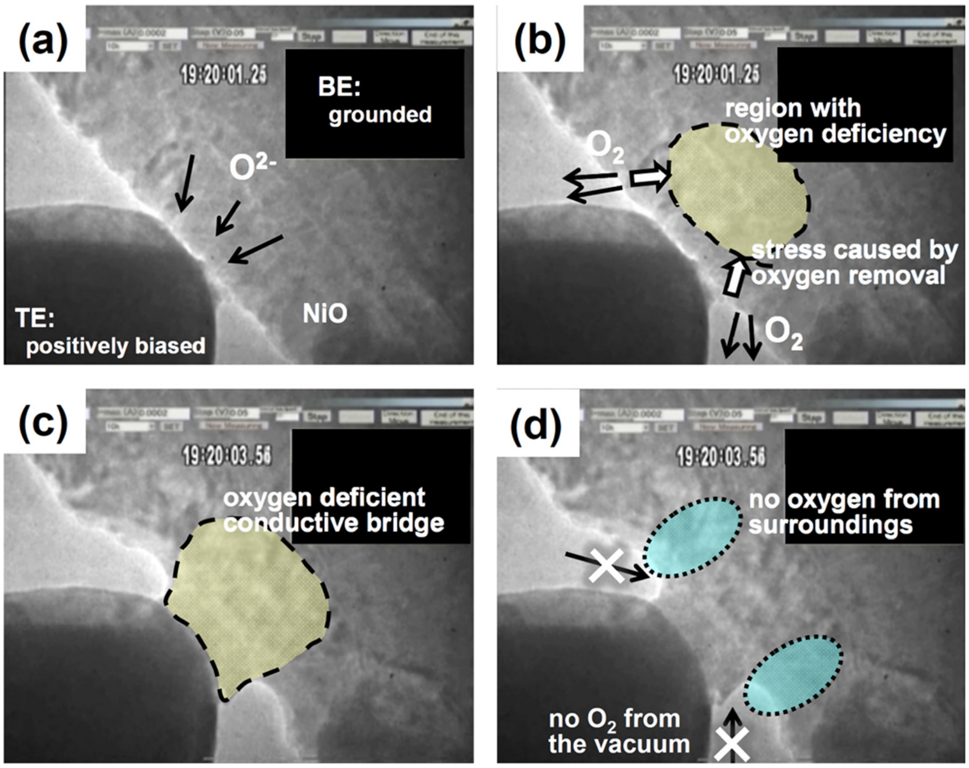

FIG. 6. Model of forming occurred inside TEM instrument. (a) Oxygen migrates to positively biased TE. (b) Oxygen deficient region was formed within ReRAM layer, and concentrated oxygen diffuses into vacuum when forming occurs. (c) Only oxygen deficient bridge remains. (d) Because of slight melt of ReRAM material around bridge, no oxygen for reset can be served. In addition, the vacuum circumstance cannot serve oxygen to the bridge.

ReRAM switching is based on the redox reaction. It was reported that the redox reaction at Pt/NiO interface contributes to the ReRAM switching[45] as reported in other materials.[38,39] After realization of *in-situ* forming-reset-set processes, composition analysis within filaments, especially at the vicinity of the Pt/NiO interface, will make clear information on the switching mechanism.

Although the forming process was clearly recognized, the reset operation was not found in the TEM instrument where the ambient is a vacuum. To investigate the reason of this result, we fabricated NiO/Pt/SiO$_2$/Si sample and I-V measurements were performed in air and in vacuum by using a Pt-Ir probe as the top electrode. The switching sequence of the forming-reset-set was recognized, when the Pt-Ir/NiO interface was exposed to air. On the other hand, no reset was recognized in vacuum. After vacuum breakage, the reset-set operation was recovered. Based on these results outside of the TEM instrument, forming without the reset operation during the *in-situ* TEM experiments were understood as follows. In the forming process inside of the TEM instrument, migrated oxygen to the Pt-Ir probe is thought to diffuse into a vacuum without remaining at the vicinity of the Pt-Ir/NiO interface, and it does not come back to the interface region. Because of this, the conductive filament could not be oxidized, and the reset process was not realized. Oxygen and/or water vapor play an important role in ReRAM switching. For continuous operation of the unipolar ReRAM of NiO, keeping oxygen around the conductive filament is important.

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