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Thermal properties of NiO_y resistor practically free from the 'forming' process

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1. Introduction

It is expected that embedded flash memory based on floating gate technology will reach its scaling limit in the near future. Among the different nonvolatile memories that are alternative to it, resistive random access memory (ReRAM) consisting of a binary transition metal oxide (TMO) such as NiO and TiO_2 is suitable for practical use, since it contains CMOS compatible materials and has a simple composition. Since they wiped out the conventional 'negative' image of dielectric breakdown (DB), they have also attracted attention. The resistance switching property of TMO-ReRAM develops after a 'forming' process, which is similar to DB, and nevertheless shows excellent performance, such as a set/ reset cycling endurance of more than 10^6 and good data retention at high temperature.[1] However, what happens during the 'forming' process is not clarified yet. To clarify the switching mechanism of TMO-ReRAM, understanding the role of the 'forming' process is considered to be crucial.

In this paper, we fabricated Pt/ NiO_y/ Pt structures practically free from the 'forming' process, which means that the *I-V* properties of their 'forming' and 'set' processes agreed well with each other. Their thermal properties suggested that 'forming' has a subtle but intrinsic meaning to develop the resistance switching property of TMO-ReRAM.

2. Experiment

We deposited Ni (Ti) film on a Pt bottom electrode by the rf sputtering method, and then oxidized it into NiO_y (TiO_x) by annealing at 360 °C (550 °C) in flowing O_2 gas. Rutherford backscatter spectroscopy showed that $y = 0.88 \pm 0.05$ and $x = 2.04 \pm 0.1$. All the thicknesses of the NiO_y and TiO_x films used in this study were 60 nm. Pt top electrodes with 200 μm diameter were deposited on the surface of the TMO layer by the dc sputtering method using a shadow mask. *I-V* property and the current-time (*I-t*) property at constant voltage were measured using a semiconductor parameter analyzer (Agilent 4156A).

3. Results and Discussion

Figure 1 (a) shows *I-V* properties of the 'forming' (open squares), 'reset' (open circles) and 'set' (open triangles) process of Pt/ NiO_y/ Pt. Here, 'reset' and 'set' are the resistance switching from the low resistance state (LRS) to the high resistance state (HRS) and that from HRS to LRS, respectively. The *I-V* property of the 'forming' process agreed well with that of the 'set' process, showing that the 'forming' process is practically unnecessary. This is quite opposite to the case of Pt/ TiO_2/ Pt as shown in Fig. 1 (b), in which the difference between the resistance before 'forming', R_{form}, and that in HRS, R_{HRS}, is more than 10^5 at 0.5 V. As shown in the inset of Fig. 1 (a) and (b), the image of the conductive atomic force microscopy (CAFM) of NiO_y before 'forming' shows that NiO_y consists of a grain structure and the current easily flows through the grain boundaries, whereas the CAFM image of TiO_x before 'forming' shows that the whole area is highly insulating. Here, the bright area shows the conductive area. The existence of the basically leaky region is considered to make the practical 'forming' process of NiO_y unnecessary.

Figure 2 (a) shows the dependence of R_{LRS} on temperature, T (= 25- 130 °C). R_{LRS} (T) shows the negative temperature coefficient, that is, $dR/dT < 0$, which is different from the positive dR/dT observed in TiO_2[2] and in NiO[3] for $T < 300$ K. As shown in the inset of Fig. 2 (a), although R_{LRS} decreased with increasing the current compliance, I_{comp}, negative dR/dT were observed independent of I_{comp} from 10 to 30 mA. This suggests that the current path in LRS does not consist of the metal, such as that separating out of Ni atoms[4], but consists of $NiO_{y-\delta}$ ($y \neq \delta$), of which the oxidation degree deviates from that of NiO_y by δ. On the other hand, Fig. 2 (b) shows R_{form} (T) (open circles) and R_{HRS} (T) (open triangles). They agreed well with each other for all measurement regions of temperature, showing that the temperature dependences of their resistivities are almost the same. They followed the Arrenius equation and estimated thermal excitation energies, Δ of both of them was ~0.3 eV, which agreed relatively well with the Δ of ~0.1 eV estimated for HRS of NiO at low temperature.[3]

Figure 3 (a) shows R_{HRS} (t)s and R_{LRS} (t)s with the baking temperature, T_{bake}, of 160 °C, where t is the baking time. Seven samples were measured each for LRS and HRS, and all of them stayed in their resistance states at 0 hour. The ratio of R_{HRS} to R_{LRS} was retained at more than 10 until 88 hours. Samples which had been programmed to LRS retained their resistances at 0 hour, whereas those programmed to HRS kept on increasing gradually, except for two samples, which showed a gradual decrease of resistance to the LRS. The increase of resistance with time was observed also in TiO_2[5].

In the case with T_{bake} = 250 °C as shown in Fig. 3 (b), all the samples which had been programmed to LRS retained their initial resistance as well as the case with T_{bake} = 160 °C. On the other hand, the resistances of the samples which had been programmed to HRS showed more notable dependence on t compared with the case with T_{bake} = 160 °C. Although all the samples stayed in HRS until 1 hour, after that, resistances changed to LRS from sample to sample and six samples out of seven changed to LRS until 88 hours. They also showed a tendency to increase until the onset of the change to LRS. The resistance of the sample, which stayed in HRS until 88 hours, increased to a value that was 10^2 times larger than its initial value. We also confirmed that thermally changed low resistance can be 'reset' back to HRS by applying a certain voltage. Therefore, it is suggested that LRS is more stable than HRS, at least at 250 °C, and that 'set' takes place thermally.

What about the samples before 'forming'? Two dotted lines in Fig.3 (b) show R_{form} (t) with T_{bake} = 250 °C. Although R_{form}

(t) agreed well with R_{HRS} (t), R_{form} did not change to LRS. We measured ten samples before 'forming', however none of them ever changed to LRS. Therefore, it is thought that the 'forming' process plays an intrinsic role even in Pt/ NiO_y/ Pt, which is practically free from 'forming'.

4. Conclusion

We studied the thermal properties of Pt/ NiO_y/ Pt, in which I-V properties of the 'forming' and the 'set' process agreed well with each other. R_{LRS} (T) showed negative dR/ dT and suggested that the current path in LRS consists of $NiO_{y-\delta}$. On the other hand, R_{LRS} (t) and R_{HRS} (t) with T_{bake} = 250 °C showed that LRS is more stable than HRS, at least at 250 °C, and 'set' process took place thermally. Although the dependence of R_{form} and R_{HRS} on both T and t agreed well with each other, R_{form} never changed to LRS thermally. This shows that subtle change, which is required to develop the resistance switching property, is caused during the 'forming' process.

References

[1] I. G. Baek, M. S. Lee, S. Seo, M. J. Lee, D. H. Seo, D.-S. Suh, J. C. Park, S. O. Park, H. S. Kim, I. K. Yoo, U-In Chung and J. T. Moon, Tech. Digest IEDM 2004, p. 587.

[2] K. Kinoshita, M. Aoki, Y. Sugiyama, and H. Tanaka, proceedings of IEEE NVSM Workshop 2006, pp. 84-85.

[3] M. G. Kim, S. M. Kim, E. J. Choi, S. E. Moon, J. Park, H. C. Kim, B. H. Park, M. J. Lee, S. Seo, D. H. Seo, S. E. Ahn, and I. K. Yoo, Jpn. J. Appl. Phys. **44**, vol.42, L1301 (2005).

[4] J. F. Gibbons and W. E. Beadle, Solid-State Electron. **7**, 785 (1964).

[5] B. J. Choi, D. S. Jeong, S. K. Kim, C. Rohde, S. Choi, J. H. Oh, H. J. Kim, C. S. Hwanga, K. Szot, R. Waser, B. Reichenberg, and S. Tiedke, J. Appl. Phys. **98**, 033715 (2005).

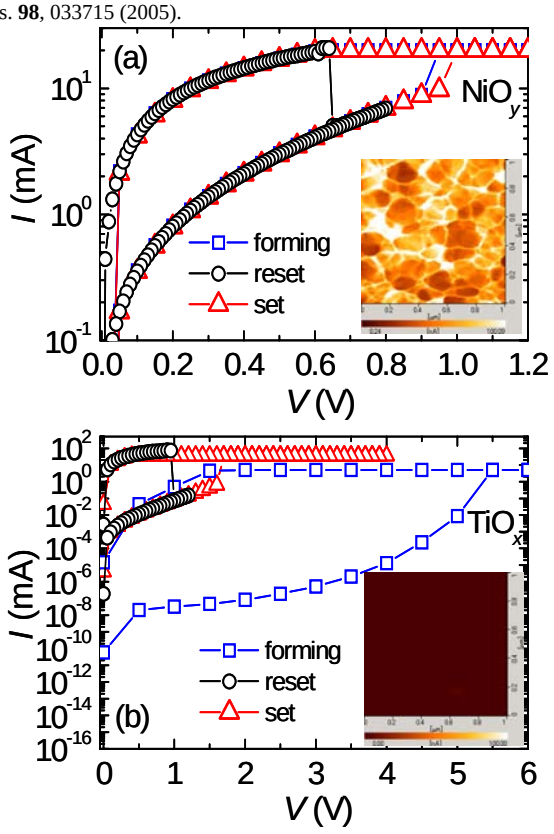

Fig.1 I-V properties of Pt/ NiO_y/ Pt (a) and Pt/ TiO_x/ Pt (b) during the 'forming' (open squares), the 'reset' (open circles) and the 'set' (open triangles) process. Insets (a) and (b) show CAFM images of NiO_y and TiO_x, respectively. The bright area shows the conductive area.

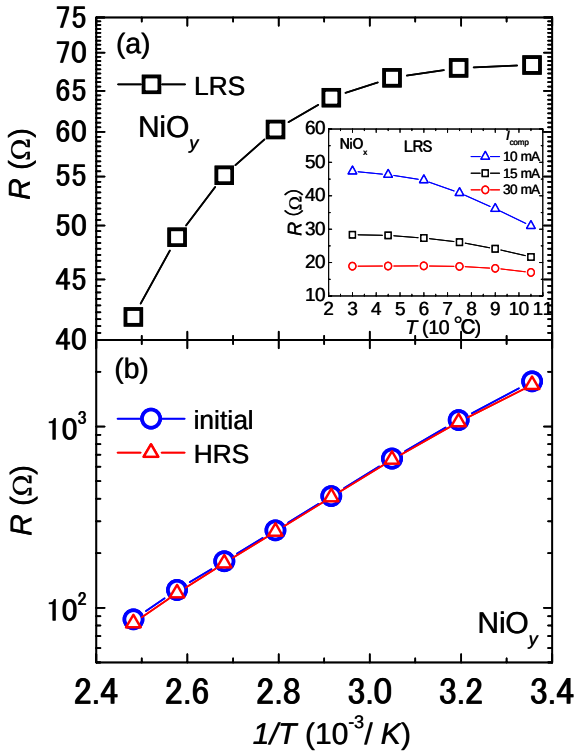

Fig. 2 Dependences of R as a function of 1/ T for LRS (a), for initial state, which is a state before 'forming' (open circles in (b)) and for HRS (open triangles in (b)). Inset of (a) shows R_{LRS}(T) for each I_{comp}.

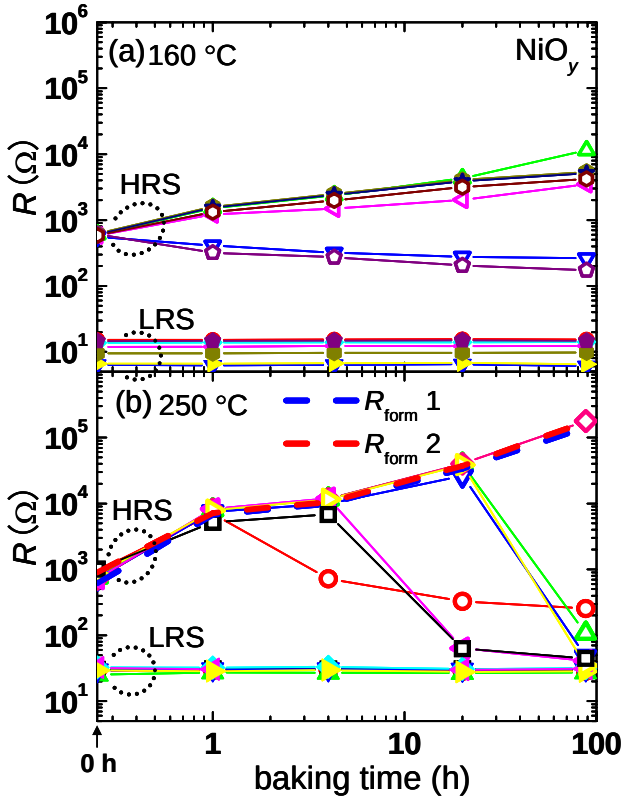

Fig.3 R_{HRS} (t)s and R_{LRS} (t)s with the baking temperature, T_{bake}, of 160 °C (a) and 250 °C (b), where t is the baking time. Two dotted lines in (b) show R_{form} (t)s with T_{bake} = 250 °C, where R_{form} is the resistance before the 'forming' process. Although R_{HRS} changed to LRS with t, R_{form}s never changed to LRS.