Extremely small test cell structure for resistive random access memory element with removable bottom electrode

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We established a method of preparing an extremely small memory cell by fabricating a resistive random access memory (ReRAM) structure on the tip of a cantilever of an atomic force microscope. This structure has the high robustness against the drift of the cantilever, and the effective cell size was estimated to be less than 10 nm in diameter due to the electric field concentration at the tip of the cantilever, which was confirmed using electric field simulation. The proposed structure, which has a removable bottom electrode, enables not only the preparation of a tiny ReRAM structure but also the performance of unique experiments, by making the most of its high robustness against the drift of the cantilever. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4867072]

NAND flash memory will face a miniaturization limit after the 20-nm generation.[1] In this environment, the development of a next generation memory that is suitable for miniaturization is required; one of the best candidates is resistive random access memory (ReRAM). ReRAM has advantages in terms of miniaturization because of its very simple structure, which is constructed simply by sandwiching a transition metal oxide (TMO) film between the top and the bottom electrodes (TE and BE).[2,3] In addition, ReRAM has several merits such as a fast switching speed,[4,5] good endurance,[6,7] and good data retention.[8] In terms of practical uses of ReRAM, a clarification of the characteristics of a single filament confined in a tiny cell is important. As one of the simplest ways to prepare a tiny cell with an area comparable to the size of the filament, a method of constructing a ReRAM (TE/TMO/BE) structure by contacting the TMO/BE structure with the Atomic Force Microscope (AFM) cantilever that works as a TE has been used.[9–12] However, in this structure, the observation of the same filament for a long time is impossible due to the influence of the cantilever drift, much less re-observation of the same filament after moving the cantilever once.

In this paper, we propose a method of preparing an extremely small ReRAM cell, which has the high robustness against the cantilever drift, by using an AFM cantilever. By depositing a transition metal oxide film on the tip of a cantilever and by contacting the bottom electrode with the cantilever, a tiny ReRAM structure can be constructed at the contact area. Since the filament is formed in the TMO film and moves with the cantilever drift, this method has the high robustness against the cantilever drift compared with the conventional structure[9–12] and enables one to perform a unique experiment to verify the presence of oxygen pools in an anode.

A Pt film with a thickness of 20 nm was deposited on an AFM cantilever with a tip radius of 50 nm (Hitachi High-Technologies, SI-DF3-R(100)) as the TE, followed by the deposition of a NiO film with a thickness of 15 nm as a memory layer at room temperature using the DC magnetron sputtering method. During NiO deposition, the pressure of $Ar + O_2$ gas was maintained at 0.5 Pa ($Ar:O_2 = 0.42:0.08$). A Pt/NiO/Pt structure was formed by contacting a Pt-BE on a SiO_2/Si substrate with a Pt/NiO structure formed on the tip of the cantilever, as shown in Fig. 1(a). Current-voltage (I-V) measurement was performed in the contact mode of the AFM (Hitachi High-Technologies, E-sweep) using a source-measure unit (SMU, Keithley 236). A bias voltage was applied to the bottom electrode, whereas the cantilever (that is, the top electrode) was grounded. The electric field distribution at the tip of the cantilever was calculated using an electric field simulator based on the finite element method (Murata Software, Femtet).

Figure 2 shows the advantage of our proposed structure over the conventional structure.[9–12] Figure 2(a) shows the conventional structure, in which NiO is sputtered on a Pt-BE and the cantilever that is used as a TE comes into contact with the NiO surface. A filament is formed in the NiO, indicating that a filament is present to the side of the Pt-BE in this structure. Therefore, the filament under measurement is easily lost because of the drift of the cantilever. Figure 2(b) shows our proposed structure, in which a filament is present to the side of the Pt-TE. Because the filament under measurement moves with the drift, we can consistently use the same filament. Figures 2(c) and 2(d) show the time dependence of resistance in the low resistance state for the conventional structure and our structure, respectively. Red circles, blue squares, and orange triangles show time dependences of resistances for three samples which were prepared under the same conditions. The resistance became high within 2–3 min, as shown in Fig. 2(c). This increase in the resistance is attributed to the drift of the cantilever, as a conductive filament is still observed after the measurement, as shown in the inset of Fig. 2(c). On the other hand, the resistance was maintained at a low resistance value for more than 30 min, as shown in Fig. 2(d). This result indicates the high

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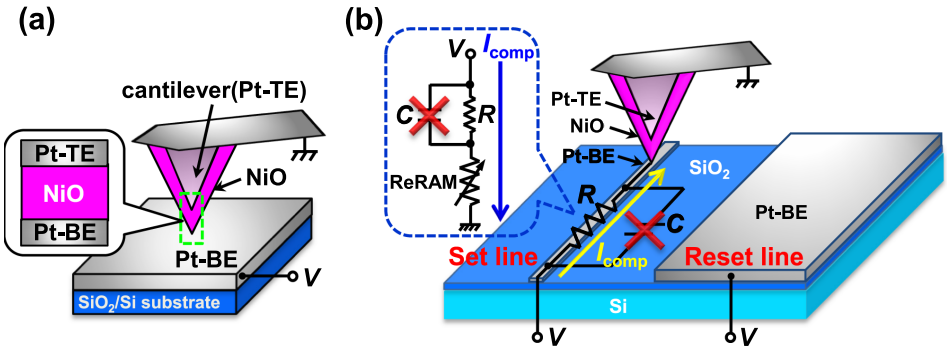

FIG. 1. (a) Tiny ReRAM structure fabricated on the tip of a cantilever of an AFM. (b) Set-line with low wiring capacitance and high resistance and reset-line with low resistance.

robustness of our structure against drift compared with the conventional structure. In addition, we confirmed that all the data written were retained after moving the cantilever to another location on the Pt-BE, regardless of resistance (low or high resistance state) and writing bias polarities. Therefore, the position of the cantilever on the BE can be changed after every measurement, without losing the filament being measured.

We observed *I-V* characteristics (data not shown) of the tiny ReRAM structure that was formed between the cantilever and the Pt-BE with an area and thickness of 14 mm $\times$ 14 mm and 100 nm, respectively. However, although both set and reset were confirmed to have occurred, the reset current was much greater than the compliance current when using a current limiter built into the SMU. In this case, the reset current was several mA, whereas the compliance current was 100 μA. After *I-V* measurement, the melting of the tip of the cantilever (inferred to be caused by the large reset current) was confirmed, as shown in Fig. 3(b). A secondary electron image of an as-prepared sample is shown in Fig. 3(a), for comparison. Therefore, reducing the reset current is necessary. Previously, we reported that the reset current is comparable to the maximum current flowing through the ReRAM element during the set process. If a large parasitic capacitance exists between the ReRAM and the current limiter, a large transient current flows through the ReRAM at the moment of set switching, and thus, the reset current becomes large. Therefore, reducing the transient current by reducing the parasitic capacitance is crucial to reducing the reset current.[13] To reduce the reset current, we formed two types of liner electrodes on the same substrate as shown in Fig. 1(b). One electrode is narrow, so as to reduce the wiring capacitance; the electrode is thin to make the resistance high so that we can use the electrode as a current limiter for setting the compliance current during the set process. By setting the thickness to less than 5 nm and the width to 10 μm, the resistance and the wiring capacitance became 100 kΩ and 30 pF, respectively. Hereafter, this electrode is referred to as a set-line. On the other hand, another electrode, one that is wide and thick, is used for reset functionality and is hereafter referred to as a reset-line. First, the cantilever came into contact with the set-line and was set to the low resistance state. Next, the cantilever moved to the reset line and was reset to the high resistance state. Forming, reset, and set were confirmed to have occurred, where forming is the common effect of ReRAM that is similar to dielectric breakdown, and the resistance switching property develops after it. In particular, the reset current decreased significantly to a value comparable to the compliance current of 100 μA. No morphological changes were observed after the *I-V* measurement, as shown in Fig. 3(c). This result indicates that a procedure to operate the tiny ReRAM structure with a low operating current was determined by the selective use of set- and reset-lines for set and reset processes, respectively.

To estimate the effective cell area of this structure, we carried out electric field simulation using the finite element

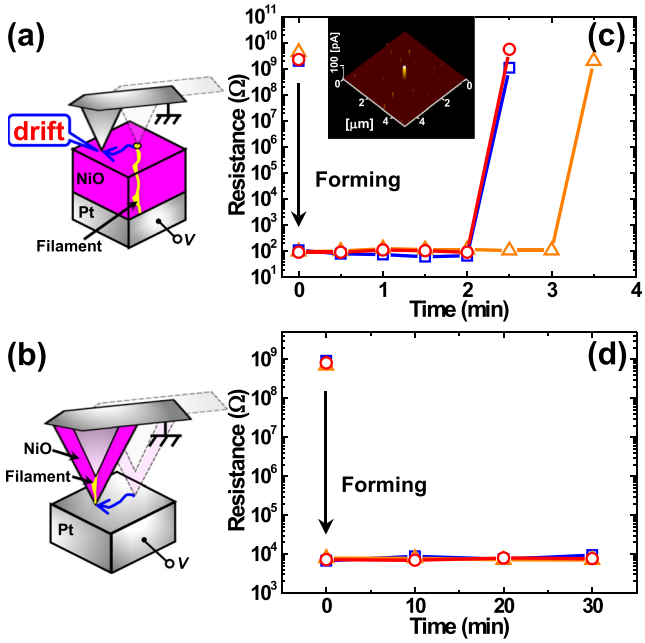

FIG. 2. (a) Conventional structure: NiO sputtered on a Pt-BE. (b) Proposed structure: NiO is sputtered on the cantilever used as a TE. Time-dependence of resistance in low resistance state in (c) the conventional structure and (d) the proposed structure, where red circles, blue squares, and orange triangles show time dependences of resistances for three samples which were prepared under the same conditions. The conductive filament is still observed after the measurement, as shown in the inset of Fig. 2(c).

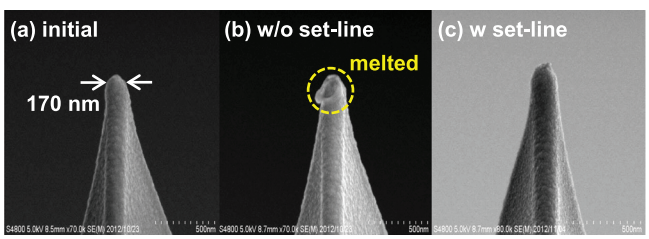

FIG. 3. Secondary electron image (a) before *I-V* measurement, (b) after *I-V* measurement without using set-line, and (c) after *I-V* measurement using set-line.

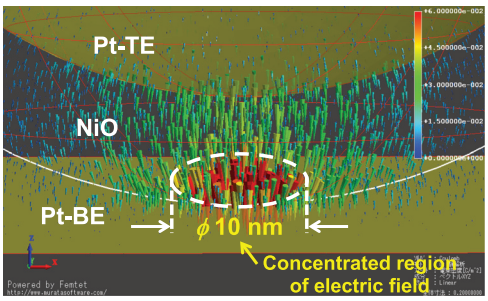

FIG. 4. Electric field distribution in the ReRAM structure calculated using the finite element method.

method. We simulated the tiny ReRAM structure using a Pt sphere covered with a NiO thin film on a Pt plate and calculated the distribution of the electric field. The electric field was concentrated near the contact point between the cantilever and the Pt-BE, as shown in Fig. 4. The electric field intensity had its maximum at the center of the contact area ($x = 0$ nm) and decayed to $1/e$ of the maximum value at $x = 5$ nm. Therefore, the effective cell area is estimated to be 10 nm in diameter (ϕ10 nm) when the radius of the Pt-coated cantilever and the thickness of the NiO ($\varepsilon = 11.9$ (Ref. 14)) layer were 70 nm and 15 nm, respectively. If we use a cantilever with a tip of radius of 40 nm and a NiO film with a thickness of 15 nm, the effective cell area is estimated to be ϕ8 nm. This result indicates that further miniaturization is possible when using a sharp cantilever.

Figure 5 compares the *I-V* characteristics of the tiny ReRAM structure (Fig. 5(a)) with that of the traditional sandwich structure (Fig. 5(b)). The area of the tiny ReRAM structure is ϕ10 nm, whereas the area of the traditional sandwich structure is ϕ200 μm. Despite the great difference in cell size, we cannot confirm a significant difference in the *I-V* characteristics between Figs. 5(a) and 5(b). In both cases, both reset and set occurred independently of the polarity of the applied voltage. This result shows a very high repeatability of resistive switching characteristics of the ReRAM element, regardless of the device size.

Models in which resistive switching is caused by thermally activated oxygen ions migration are being widely received.[9,15–18] Many of these models require the anode to act as an oxygen reservoir.[9,15,16] In these models, by applying a positive voltage to the top electrode, oxygen ions move into the anode and oxygen vacancies are introduced into the metal oxide layer. As a result, filaments consisting of oxygen vacancies are formed and switch to the low resistance state. To reset these filaments, the oxygen vacancies must be repaired by the oxygen ions stored in the anode. Therefore, finding the oxygen pool in the anode is important for the verification of the models. We performed a unique experiment to verify the presence of an oxygen pool in the anode utilizing a removable BE structure. First, a positive bias was applied to the set-line in air until the occurrence of the forming, as indicated by the orange squares in Fig. 6. Next, the cantilever was removed from the set-line and only the BEs were annealed in vacuum (1.0×10^{-3} Pa) at 300 °C (= 573 K) for 10 min to desorb the oxygen and water from the Pt surface. After annealing, the cantilever was moved to the reset-line and a positive bias was applied to the reset-line at room temperature. The *I-V* characteristics are indicated by red triangles in Fig. 6. The occurrence of reset was confirmed. Here, it should be noted that the oxygen molecules and water adsorbed on the Pt(111) surface desorbed above 150 K and 180 K in vacuum, respectively, whereas atomic oxygen desorbs at temperatures above 600 K.[19] Therefore, after annealing the BEs at 300 °C (573 K) in a vacuum, the oxygen molecules and water entirely desorb from the Pt surface, whereas atomic oxygen remains. The saturation concentration of the adsorbed oxygen atoms is reported to be approximately 3.8×10^{14} atoms/cm^2 corresponding to one oxygen atom per four surface platinum atoms.[19] These results indicate that reset is caused by either oxygen ions inside the NiO film as reported in Refs. 17 and 18 or oxygen atoms on the Pt surface (3.8×10^{14} atoms/cm^2 = 1 oxygen atom/4 surface platinum atoms).

Finally, after moving to the set-line again, the success of the set operation was confirmed (blue circles in Fig. 6). We

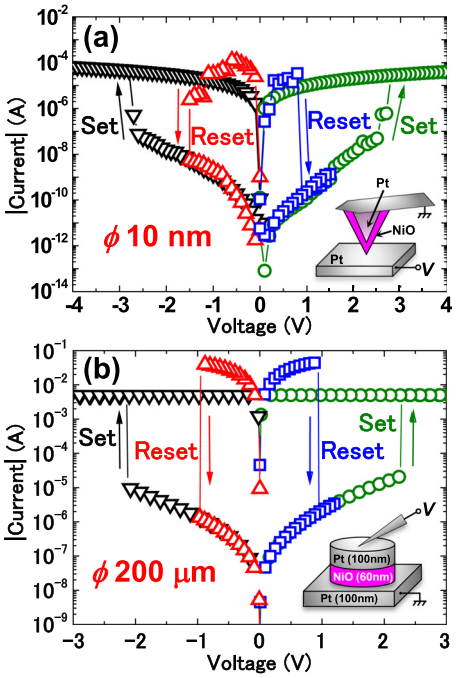

FIG. 5. *I-V* characteristics of Pt/NiO/Pt structures with areas of (a) ϕ10 nm and (b) ϕ200 μm.

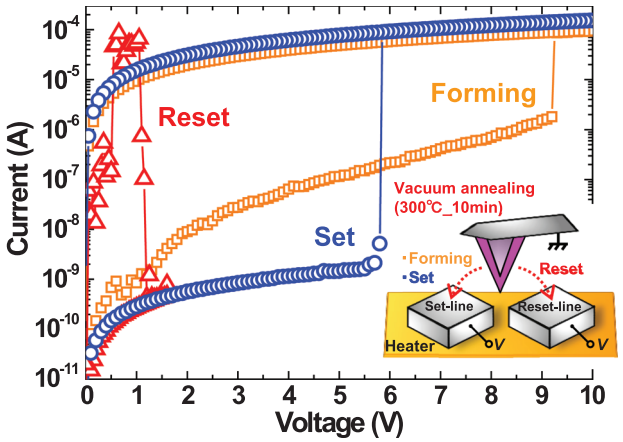

FIG. 6. *I-V* characteristics for successive forming, reset, and set processes, which were measured at different points for every measurement by applying positive bias to the BE.

often confirm that the resistance in high resistance state (R_{HRS}) becomes higher than the resistance in initial resistance state (R_{ini}) during switching cycles, in the samples used in this study. The similar phenomenon was also observed in 10×10 nm^2 size ReRAM elements by Govoreanu *et al.*[20] This can be understood based on parallel resistance model, in which the total resistance (R_{total}) is given by the parallel connection of the resistance of a filament (R_{fila}) and that of a film excluding the filament (R_{excl}), namely, $1/R_{total} = 1/R_{fila} + 1/R_{excl}$.[21] In small samples, the device area is comparable to the cross-sectional area of the filament, and, thus, the resistance excluding the filament, R_{excl}, becomes large enough to satisfy the relation of $R_{excl} \gg R_{ini}$. In this case, R_{fila} becomes dominant in R_{total}. Therefore, the relationship that $R_{HRS} > R_{ini}$ can be satisfied due to the dispersion of the R_{HRS}^{fila}, where R_{HRS}^{fila} represents R_{fila} in high resistance state. Here, the dispersion of R_{HRS}^{fila} is caused by the dispersion of δ in the composition of filament region, $NiO_{1-\delta}$, namely, the oxidation degree of the filament. When δ approaches zero (stoichiometric composition) more closely than δ for initial state because of excess oxidation of the filament in reset process, R_{HRS}^{fila} ($\approx R_{HRS}$ in this case) can be higher than R_{ini}.

In conclusion, we have established a fabrication method for tiny ReRAM structures using an AFM cantilever. The proposed structure is highly resistant to drift and movement and enables to keep observing the same filament for a long time. We also established a set-procedure to reduce the reset current using a thin, narrow linear electrode, and succeeded in avoiding serious damage to the cantilever. The effective cell area was estimated to be 10 nm in diameter on the basis of electric field simulation. We confirmed that there was no difference between Pt/NiO/Pt structures with areas of $\phi 10$ nm and $\phi 200\,\mu$m, strongly suggesting applicability to miniaturization. By utilizing the removable BE structure, we have shown that reset can occur via oxygen atoms on the Pt surface (3.8×10^{14} atoms/cm^2) or oxygen ions inside the NiO film. The proposed method provides further insight into the resistive switching phenomena of a single filament.

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