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The influence of annealing temperature on ReRAM characteristics of metal/NiO/metal structure

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Abstract. The resistive switching of NiO sandwiched between Pt bottom and top electrodes are formed by thermal oxidation at the temperature from 300°C to 800°C. The ReRAM characteristics are investigated from the view point of practical applications. The stable and uniform formation of NiO films are revealed by XPS analysis and the chemical compositions of NiO are almost independent of oxidation temperatures. However, the forming voltages of the film prepared at higher oxidation temperature are scattered and reach to high values. This fact indicates that the forming process occurs at the weak spot, and the density of the weak spot is low in the film formed at higher temperature. As a result, the NiO prepared at lower temperature shows stable and lower forming voltages.

Keywords : Resistance switching memory, ReRAM, Nonvolatile memory, NiO, Binary Metal oxide

1. Introduction

Resistance switching random access memory (ReRAM) has attracted much attention for the next generation memory due to its potential for high density, fast response, low power consumption, and nonvolatility. Resistance switching controlled by external voltage was founded in perovskite type oxide, which shows so-called bipolar type switching[1,2]. Many kinds of transition metal oxides have been reported as ReRAM materials: such as NiO, TiO_2, CoO, CuO, ZnO[3-7]. Although the resistance switching phenomena and their reproducibility were reported, their switching mechanism has not clearly shown[8]. One of the biggest problems of ReRAM for practical use is that the switching mechanism is unknown. Among many kinds of materials, NiO is the great candidate for practically usable material because of its stable structure and relatively high on/off resistance ratio as a ReRAM device[9,10]. The material acts as ReRAM with a simple Metal electrode/Oxide/Metal electrode (MOM) structure and shows so-called monopolar switching characteristics. Some reports imply the formation of Ni filaments between top to bottom electrode[11]. Then the switching occurs due to the connection and disconnection of the filament caused by the reduction and oxidation reaction of Ni filament, respectively. Usually, NiO is initially in the high resistance state (HRS), in which there is no filament. So, for the operation of ReRAM, it is well known that the forming process is needed to form the filament, which can be achieved by applying relatively high voltage to the MOM structure. Then, resistance switching between the low resistance state (LRS) and HRS can occur at relatively low applying voltages. The process changing from HRS to LRS is called SET process and that from LRS to HRS is called RESET process. In general, forming voltage is higher than SET voltage, though both of these two operations induce a transition from HRS to LRS. It is usable that the forming voltage is as low as SET voltage. Here, we investigated the fabrication process of NiO films to achieve stable and lower forming voltage.

2. Experiments

Fabricated ReRAM devices have a simple MOM structure formed on a thermally oxidized Si (100) wafer. We used a 100-nm-thick Pt film as a bottom metal electrode that was formed by radio frequency (RF) sputtering with adhesive of thin Ti layer on the wafer. Then, a 100-nm-thick Ni film was deposited on Pt/Ti/SiO_2/Si by RF sputtering at room temperature[12]. NiO thin films were formed by annealing the samples in air at various temperature from 300°C to 800°C. The annealing time was three minutes. Finally, Pt top electrodes were deposited by RF sputtering. The area of the electrodes was 100 × 100 μm^2, 200 × 200 μm^2, 500 × 500 μm^2, and 1 × 1 mm^2. The depth profiles of the compositions of the NiO films were investigated by using XPS (X-ray photoelectron spectroscopy). The electrical property of NiO ReRAM characteristics was measured on a probe station using YOKOGAWA GS 610 source measure unit at room temperature in air.

3. Results and Discussion

The depth profiles of the NiO film formed at 700°C are shown in figure 1. A very thin NiO film was formed at the surface of Ni film when the annealing temperature was lower than 400°C, and an about 30-nm-thick NiO film was formed on the surface of the Ni film at 500°C. As shown in figure 1, a uniform NiO film, in which all the Ni layer was oxidized completely, was formed when the annealing temperature is higher than 600°C. Ni 2p spectra measured by XPS for the NiO films oxidized at various temperatures are shown in figure 2. The measurement was done just after two-minutes sputtering of the surface in order to avoid surface contamination layer of the film. The spectra show a peak between 854 eV and 875 eV corresponding to the typical Ni 2p 3/2 spectra of NiO[13,14]. It is clearly shown that the peak shapes are almost the same in spite of the difference in the oxidation temperature. The result indicates that the thermal oxidation of Ni film forms stable NiO films.

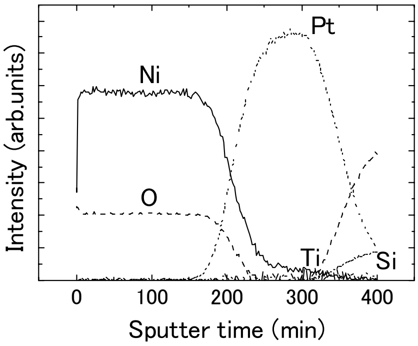

Figure 1. Depth profile of NiO film annealed at 700°C measured by XPS.

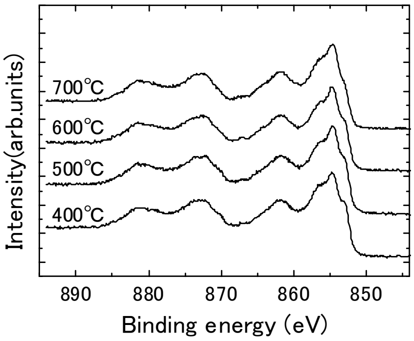

Figure 2. XPS Ni 2p spectra for NiO films formed at various temperatures.

In the forming process performed to change the initial HRS to LRS, we scanned the voltage applied to the top Pt electrode by setting the current compliance of 2mA. In the RESET process for returning from LRS to HRS, we scanned the voltage without the current compliance. Then the SET process was performed by same method as the forming process to change HRS to LRS. Figure 3 shows typical I-V characteristics measured on the NiO film formed at 600°C according to this process. The I-V curve showed clear monopolar-type ReRAM characteristics. This ReRAM characteristics were obtained from the NiO films oxidized at the temperature higher than 500°C. As mentioned above, in the NiO films oxidized at the temperature higher than 600°C, all of the initial Ni layers were oxidized, which provided the NiO films with the same thickness because the initial Ni film thickness were the same (100 nm). The initial resistances of NiO films formed at various temperatures are shown in figure 4 as a function of electrode area. It is reasonable that the resistances of NiO films formed at the same temperature were almost inverse-proportional to the area of electrodes. This result indicates that the film was uniform in these areas. It is also clearly shown that the resistance of the NiO films formed at higher temperatures tends to have higher resistances. The fact implies that the NiO films formed at higher temperatures have better quality as an insulator. After the forming process, the resistance at LRS became around 20-150 Ω independent on the annealing temperatures and the area of top electrodes. The reason is that LRS was thought to be realized by the filaments and has the resistance independent of areas and oxidation temperatures because the resistance may be determined by the diameter of the filament. The diameter of the filament was thought to mainly depend on the compliance current during the SET or the forming processes.

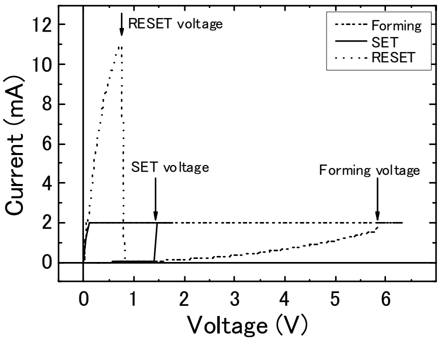

Figure 3. I-V characteristics measured during forming, RESET, and SET processes. The measured NiO film was formed at 600°C.

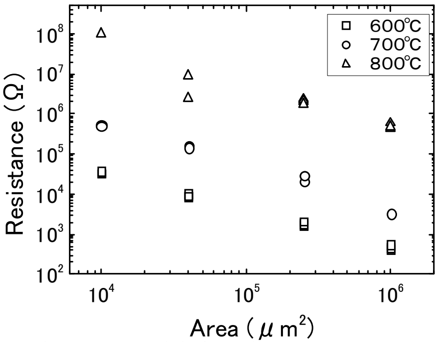

Figure 4. Initial resistance as a function of area of top electrodes for the NiO films formed at 600°C, 700°C, and 800°C.

One of the important parameters for practical use of ReRAM is the forming voltage. Figure 5(a) shows the forming voltage measured for many NiO devices as a function of oxidation temperature. The forming voltages were scattered from one device to another, and the voltage width of scattering becomes wider as oxidation temperature increased. Figure 5(b) shows the area dependence of the forming voltage. The forming voltage of NiO devices formed at 600°C was almost independent on the area of top electrodes, and had relatively low value of about 4-6 V. In contrast, the forming voltage of the devices formed at 800°C showed strange area dependence. In the wider areas, scattering width of the forming voltage was relatively narrow, and the voltages were almost the same as those of the devices formed at 600°C. However, in the smaller areas, scattering width became wide and reached about 13 V. The result of figure 5(b) suggests that the lower forming voltage site, which corresponds to a weak point or a defect sites in the NiO film, are distributed in the area. In the case of NiO formed at 800°C, the number of the site was one or zero in 10^4 μm^2. The density was not high but caused a big problem, since the forming voltage distribute much widely when we made a small area device for the practical application of ReRAM.

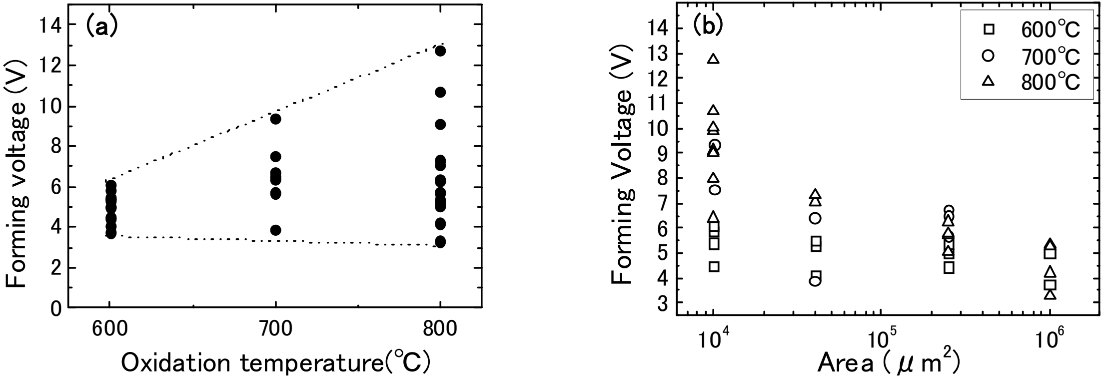

Figure 5. Forming voltage as a function of oxidation temperature (a), and as a function of area of top electrodes (b) measured for NiO film formed at 600°C, 700°C, and 800°C.

The NiO films formed at 600°C seem to have many weak spots for forming the filaments, which may be advantageous for keeping the forming voltage lower with small distribution. We can conclude that the NiO films oxidized at low temperature had better nature for suppressing the distribution of ReRAM device characteristics. But, further investigation is needed to clarify the controllability of the density of the weak spots in the NiO films. The endurance during SET/RESET cycles was measured for the device formed at 800°C. Figure 6 shows the resistance switching between LRS and HRS. The resistance ratio was kept at least 30. Although the forming voltage of NiO formed at 800°C was widely distributed, the resistance-change characteristics caused by the SET/RESET cycles were stable and almost the same as those of NiO formed at low temperature. The densities of the weak spots, which strongly control the forming process, did not affect the characteristics of the filament itself.

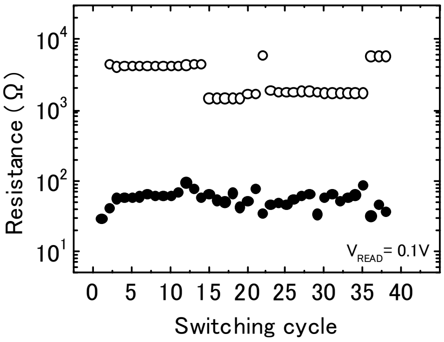

Figure 6. Switching characteristics measured by repeating SET and RESET cycles. The NiO film was formed at 800°C.

4. Conclusion

The resistance switching characteristics of NiO films formed by thermal oxidation were investigated from the view point of practical ReRAM applications. XPS analysis revealed that the NiO films were uniform and their chemical compositions were independent on the oxidation temperature. However, the initial resistances are higher for the NiO films formed at higher temperature, which implies that the higher temperature provides better quality of NiO films as an insulator. In addition, the NiO layers oxidized at high temperature contain less weak spots which supply the higher forming voltage. This causes the scattering of forming voltage of the filament. These results indicate that the control of the weak-spot density is a key issue to get lower forming voltage together with smaller distribution.

Acknowledgments

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