Control of Conducting Path in Resistive Memory Utilizing Ferritin Protein with Metal Nano Dot

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ABSTRACT

Bio-nano-process (BNP) has been proposed as promising bottom-up process to fabricate nanostructure. The application of BNP to memory devices such as resistive random access memory (ReRAM) is large interested because BNP could offer attractive solution to reduce the memory size and improve the device performance. We investigate the application of metal nano dot to ReRAM for control the filament path. Memory switching mechanism in ReRAM is supposed to be based on the formation and rupture of random nano-filament. Metal nano dot can be expected to help the formation of the confined filament and stabilized switching performance. We succeeded to localize the conductive filament by gold nano dot. The device with Pt nano dots embedded in NiO exhibit stable resistance switching.

Keywords: resistive memory, nanoparticle, ferritin, bio nano materials

1 INTRODUCTION

To overcome a scaling limit of top-down process in semiconductor devices, bio nano process (BNP) has been proposed as promising bottom-up process. The BNP provides excellent uniform nano-scalse components, selective adsorption [1, 2, 3] and self assembled structures [4] One of the nano structures is utilized by the biological molecule ferritin. They can crystallize different kind of inorganic nano-dot such as Fe-oxide, Co-oxide, Ni-oxide, PtS, inside their vacant cavity by bio-mineralization. These nano scale component are named as Bio-Nano-Dot (BND). So far, various applications using BND have been reported such as nano-dot floating gate memory and single electron transistor [5, 6, 7]. On the other hand, the resistance switching phenomena of metal-oxides such as NiO [8, 9, 10, 11], CoO [11], Fe_2O_3 [11] have been attracting because the memory size can down to an extremely small for future high density mass storage application. It was reported that resistance switching behavior in oxide film is related to the formation and rupture of a conducting path [8]. According to the proposed resistive switching mechanisms, it has been believed that the voltage stress randomly creates conductive filaments inside the NiO matrix [12]. The different filament pattern is generated in every switching cycles and it is unpredictable. As a consequence, these random filaments cause the large fluctuation of switching properties. Therefore, several studies have been carried out to improve the device performance using metallic nano dots in oxide layer [13, 14].

In this study, we investigate the application of metal nano dot to NiO-base resistive random access memory (ReRAM). We assume that the controlling of the conductive path is crucial in order to improve the performance of the resistive switching. The localized electric field at the forming process plays an important role in leading to formation of the conductive path. If the electric field is concentrated in nano scale, single conductive path can be formed along the electric field because the size of the switching path is considered approximately nano scale [15]. The metal nano dot embedded in oxide film can be expected to help the formation of the single conductive path owing to a high concentration of electric field at the region between Pt electrode and nano dot. We evaluated the effects of metal nano dot in switching operation of NiO based ReRAM.

2 C-AFM MEASUREMENT

To control the position of conductive path and confirm the path, we have fabricated NiO/Gold nano dot/n^+Si structure. The gold nano dot can be expected to help the formation of the conductive path due to the concentration of applied electric field. The gold nano dots (diameter of 15 nm) were adsorbed on n^+ Si substrate and 20 nm thick NiO film was deposited on these dots by electron beam evaporation. The cross sectional TEM image is shown in Fig. 1. Local conductivity was observed by using conductive atomic force microscopy (C-AFM) with the Pt/Ir-coated tip. Fig. 2 shows the topographic image of the

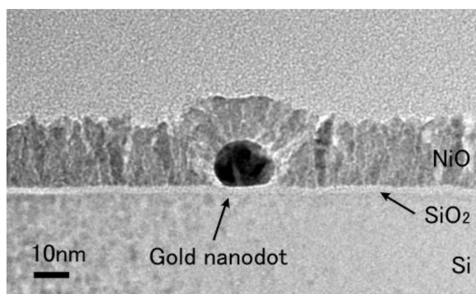
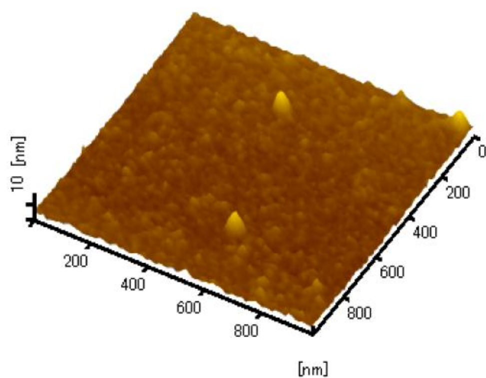


Figure 1: TEM image of the sample with gold nano dot embedded in NiO film.



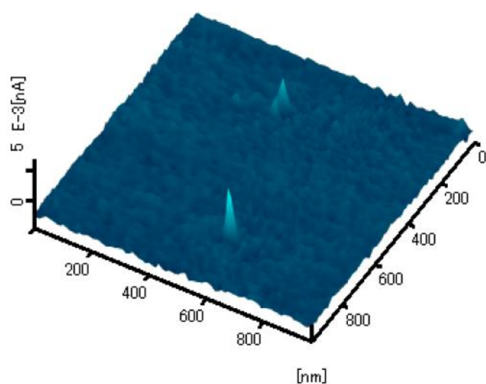


Figure 2: (a) Topographic image of conductive AFM and (b) corresponding current image.

NiO surface and corresponding current image. One can observe that the very confined nano scale current paths appeared at the surface which the gold nano dot is located. This result indicates that the gold nano dot in the NiO film can effectively control the position of the current path. The current path is also ruptured and reformed by applying appropriate voltage.

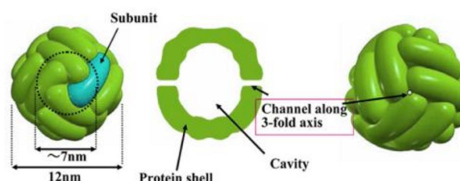
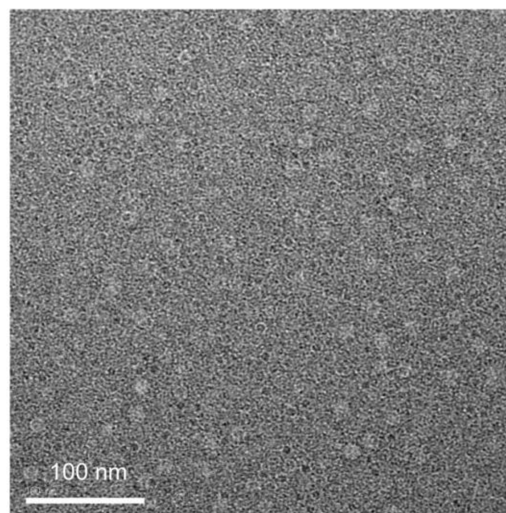


Figure 3: Structure of ferritin protein.



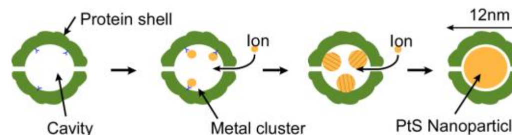


Figure 4: TEM image of ferritin protein with PtS core and schematic image of the core formation process.

3 RESISTIVE SWITCHING WITH PLATIMUM NANO DOT

3.1 Fabrication

The nano structural fabrication of the Pt nano dot (Pt-ND) in NiO film has been carried out using BNP with ferritin protein. The ferritin protein is a spherical structure with the diameter of 12 nm and 7 nm vacant cavities inside (Fig. 3). We synthesized PtS core in the ferritin cavity using the solution of 0.5 mg/ml apo-ferritin, 2 mM K_2PtCl_4, 2.6 mM $(NH_2)_2CS$, and 100 mM SPB pH 8.0 as shown in Fig.4. The formation of nano dots in ferritin cavity is written elsewhere [16, 17]. Cross sectional image of the device with the model of the filamentary conducting path in NiO film along the Pt-ND is schematically illustrated in Fig.5 (a). Figure 5 (b) shows simulated electric field image of the device with a metal nano dot. The electric field below and above the metal nano dot is enhanced. The device containing Pt-NDs was fabricated on $Pt/Ti/SiO_2/Si$ substrates as follows. First, NiO film with thickness of 3nm

was deposited by electron beam evaporation on substrate using stoichiometric NiO target. Then, the surface was cleaned by UV/ozone treatment at 115 ^{o}C for 10min. Ferritin solution with PtS core with a concentration of 5 mg/ml in pure water was dropped on NiO layer and kept for 10 min. After the adsorption of ferritin protein, UV/ozone treatment was carried out at 115 ^{o}C for 50 min in order to remove the protein shell and to help the reformation of PtS dot to Pt dot. Then the second NiO layer with the thickness of 6 nm was deposited on Pt-NDs. Finally, Pt top electrodes with the size of $20\times20\mu m^2$ were fabricated using photo lithography and lift-off process. Devices containing different density of Pt-NDs were also fabricated to evaluate the effects of the Pt-ND. The density of dots was controlled by adjusting the concentration of ferritin solution. To confirm the role of Pt-ND, control sample without dots was fabricated with the same process.

The nano structural characterization and chemical bonding state of the dot were carried out by TEM and Electron energy loss spectroscopy (EELS). The cross-sectional TEM image of the fabricated devices is shown in Fig.6 (a). The existence of the Pt nano dots was experimentally confirmed from Pt mapping image using EELS as shown in Fig.6 (b) and (c). The Pt-NDs with the diameter of approximately 3 nm were found to be embedded in the polycrystalline NiO matrix.

3.2 Results and discussion

Typical I-V characteristics of the devices with Pt-ND embedded in NiO are shown in Fig. 7. The electro-forming and set operations were performed in current controlled mode while the reset operation in voltage controlled mode. Typical unipolar type resistive switching behavior was observed in both samples with and without Pt-NDs. Figure 8 (a) shows the distribution of the high (OFF) and low (ON) resistance as a function of switching cycles. The resistance values were read at 0.5 V in each sweep. From Fig. 8 (a), the fluctuation in OFF resistance of the NiO with Pt-ND is more stabilized rather than that of the sample without dot. This stabilization of resistance is consistent with the result reported by D. C. Kim et al [18]. They reported that highly crystalline NiO confines conducting paths locally, avoiding their random formation and rupture. Some previous reports have also shown that the switching process in metal-oxide is the electro migration of oxygen vacancy or oxygen ions [8, 19, 20]. From these result, we assume that the locally concentrated

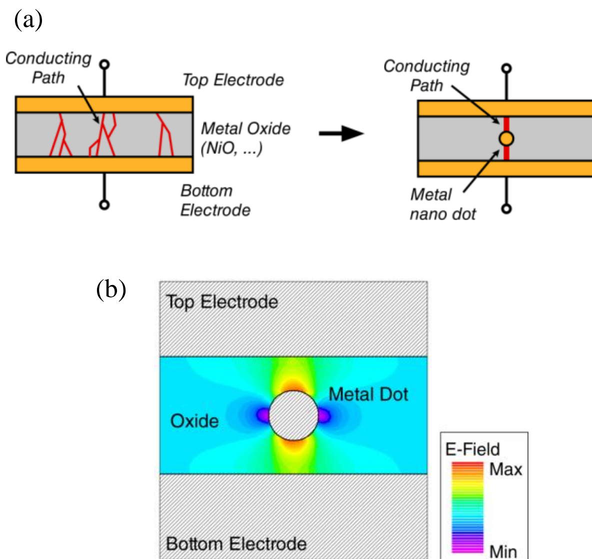


Figure 5: (a) Schematic image of cross sectional structure with and without nano dot. (b) Electric field simulation of the nano dot embedded device before forming.

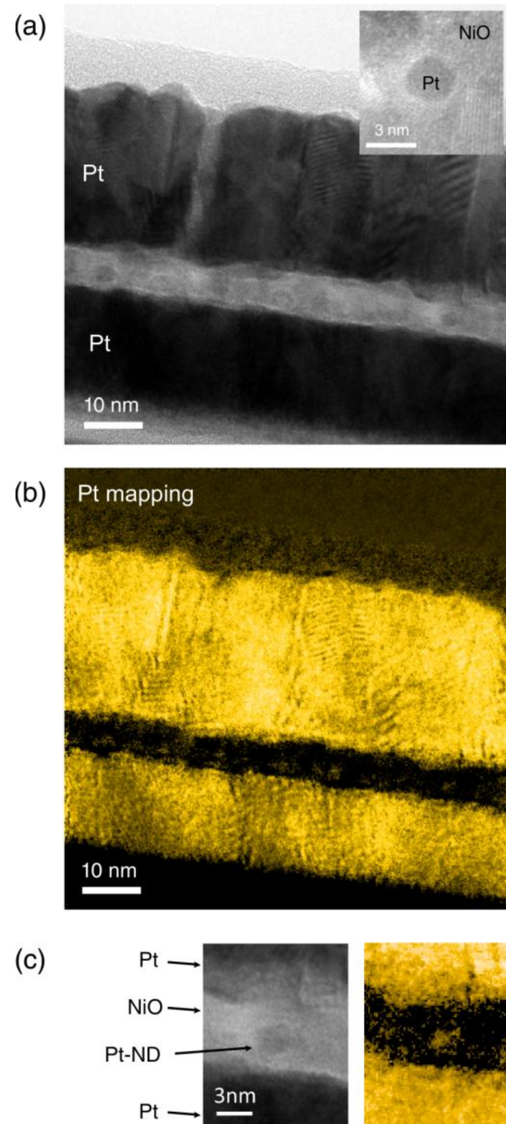


Figure 6: (a) Cross sectional TEM image of the device. (b) EELS mapping of Pt. (c) TEM image and corresponding EELS image.

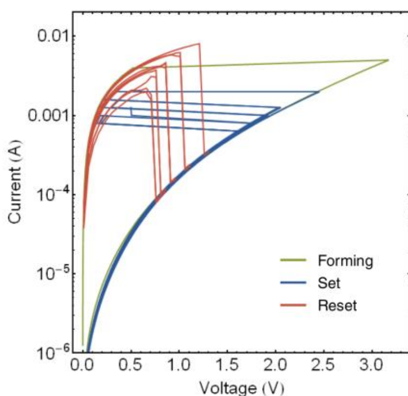


Figure 7: Typical I-V characteristics measured for the Pt nano dots embedded device.

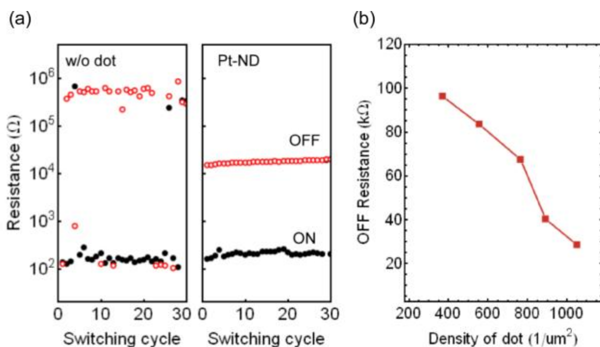


Figure 8: (a) Resistance values of the set and the reset states with and without dot. (b) OFF state resistance plotted against the density of dot.

electric field between Pt electrode and Pt-ND enhances diffusivities of oxygen vacancy or oxygen ions significantly and form a fixed conducting path along the Pt-ND. As a consequence, the fluctuation of the resistance is stabilized rather than random filament paths.

Figure 8 (a) also indicates that the OFF state markedly depends on the Pt-NDs, whereas the resistance of ON state is almost independent of the existence of Pt-NDs. Figure 8 (b) shows the result of the OFF resistance is plotted as a function of the dot density. The OFF resistance is decreased as the density increase. We also evaluated electrode size dependence of the switching resistance. The OFF resistance was decreased with electrode size, whereas the ON resistance was size independent. These facts indicate that the OFF resistance is attributable to the leakage current flowing along the Pt-NDs. On the other hand, the conductive path at ON state is locally confined along the Pt-ND. Therefore, the on/off resistance ratio in dot embedded device is improved by reducing the density of dots.

4 CONCLUSION

The resistive switching with metal nano dots embedded in NiO structure was investigated. The Pt-ND embedded ReRAM exhibits the stable unipolar resistive switching behavior owing to the controlled conducting path. Observed OFF resistance depends on the density of the Pt-NDs. The resistance of OFF state is attributed to the leakage current flowing through the Pt-NDs in NiO film. On contrast, single conducting path exists in NiO film along the Pt-ND at ON state. We believe that the nano dot utilizing ferritin protein will enable us to use it as an element of future nano devices, and BNP can provide promising nano-scaled structure for new device applications.

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