Effects of Guided Filament Formation in NiO-ReRAM Using Bio-nanoparticle

Mutsunori Uenuma^{1,2}, Takahiko Ban^{1,2}, Bin Zheng^{1,2}, Masahiro Horita^{1,2}, Yasuaki Ishikawa^{1,2}, Ichiro Yamashita^{1,2} and Yukiharu Uraoka^{1,2}

¹ Nara Institute of Science and Technology Graduate School of Materials Science, 8916-5, Takayamacho, Ikoma, Nara 630-0192, Japan Phone: +81-0743-72-60663 E-mail: uenuma@ms.naist.jp ²CREST, 4-1-8, Honcho, Kawaguchi, Saitama, 332-0012, Japan

1. Introduction

A resistive random access memory (ReRAM) has been attracting great attention as a promising next-generation memory. In the case of a NiO-based ReRAM, it is considered that a resistive change occurs with a formation and rupture of conductive nanoscale filaments in a NiO layer [2]. According to the proposed resistive switching mechanisms, many conductive filaments are randomly formed by the voltage stress inside the NiO matrix [3,4]. Additionally, an initial electroforming step is required to activate the switching property, and a nonpolar ReRAM requires a high forming voltage. Reducing the high forming voltage and the control of the position of nanoscale filament are still problems. The nanoscale filament makes it difficult to control the position precisely.

We have been studying a biological nanofabrication process, which is referred to as a "bio-nano process (BNP)" [5-7]. In this study, we applied the BNP to incorporate a gold nanoparticle (GNP) into a NiO matrix, and we investigated the effects of the GNP on ReRAM properties.

2. Fabrication and results

First, we performed conductive AFM to study the local conductivity of the GNP-embedded NiO film. We initially aligned GNPs of 15 nm diameter with 400 nm pitch on a bottom electrode using a porter protein. The porter protein is a recombinant bifunctional protein made of a ferritin subunit. The GNPs were encapsulated by the porter protein and delivered to the designated positions (Fig. 1). Then, a NiO layer of 20 nm thickness was evaporated (Fig. 2). Figure 3 show SEM images of the aligned GNPs. The detailed process is described by Zheng [8]. The c-AFM measurements were conducted. As shown in Fig. 4, the c-AFM image clearly shows the conductive spots (Filament) above the GNP.

To study the effects of GNPs in memory switching, Pt/NiO-GNP/Pt structure was produced. First, GNPs coated by the porter protein were randomly adsorbed onto a bottom electrode. Then, the NiO layer was formed (Fig. 5). Finally, Pt top electrodes were formed. Figure 6 shows the typical I-V relationships of samples with and without the GNPs, respectively. The forming voltage was reduced to nearly the same level as the set voltage. The sample with the GNPs had a relatively low forming voltage. To elucidate the conduction mechanism of the Pt/NiO-GNP/Pt memory, the differential resistances $\Delta LogI/\Delta LogV$ derived

from the LogI-LogV during the forming process were plotted (Fig. 7). The conduction behaviors in the low-voltage region are similar even in the presence of GNPs. However, in the high-voltage region (> 2.0 V), the conduction mechanism is completely different between the samples with and without GNPs, because the slope of the LogI-LogV curvature increases differently. In the sample with the GNPs, the slope markedly increases above 2.0 V. This curvature is similar to that of set process. To clarify the mechanism of forming voltage reduction, the crystalline structure was observed using a cross-sectional TEM. The NiO region without the GNPs has a fine columnar structure with a flat surface. On the other hand, irregular grain structure was observed on top of the NiO layer deposited on the GNPs. Since the grain boundary is more conductive than other regions [4] and acts as a leakage source, the lower initial resistance of the memory cell with the GNPs is attributed to the leakage current of the grain boundaries and defects above the GNPs. Additionally, it is considered that the lower forming voltage is mainly due to the creation of filament paths caused by the preexisting defects in the NiO laver above the GNPs (Fig. 8). Therefore, the highly conductive defects in the NiO layer formed by the GNPs might assist the formation of conducting filaments during the forming process [9].

3. Conclusion

We demonstrated GNP-embedded NiO-based ReRAM devices using the BNP. The location of conductive filament formation was controlled to be at the position of each GNP. The forming voltage was reduced by the defects in a highly localized region.

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References

[2] M. J. Lee, et al., Nano Lett. 9 (2009) 1476. [3] C. Park, et al., Appl. Phys. Lett. 93 (2008) 042102. [4] G. S. Park, et al., Appl. Phys. Lett. 90 (2007) 222103. [5] I. Yamashita, Thin Solid Film 393 (2001) 12. [6] S. Yoshii, et al., Appl. Phys. Lett. 95 (2009) 133702. [7] S. Kumagai, et al., Appl. Phys. Express 3 (2010) 015101. [8] B. Zheng, et. al, Chem. Phys. Lett. 506 (2011) 76. [9] M. Uenuma, B. Zheng, K. Kawano, M. Horita, Y. Ishikawa, I. Yamashita and Y. Uraoka, Appl. Phys. Lett. 100 (2012) 083105.



Fig. 1 Schematic image of bifunctional protein-coated GNP for nanoscale positioning of a GNP. The GNP with diameter of 15 nm was encapsulated by a bifunctional protein (ferritin mutant). TEM images of protein-coated GNP.

Fig. 2 Fabrication process of the GNP embedded ReRAM structure. After adsorption of protein-coated GNP, the protein shells were completely removed by UV/Ozone treatment at 110 °C for 50 min.

SEI 5.0kV X37.000 100nm WD 3.0mm Fig. 3 SEM images of controlled placement of the GNPs before formation of NiO layer. The selectively

placed GNPs with 400 nm pitch.



Fig. 4 (a) Topographic image of c-AFM and (b) corresponding current. first a 2 × 2 μ m square area (inside the dashed line) was scanned with a set bias and then the entire area (4 × 4 μ m) was scanned with a read bias. The current image inside the dashed square area showed conductive spots that correspond to the topographic image, whereas no highly conductive spots were observed outside the 2 × 2 μ m square area. (c) C-AFM images of NiO surface scanned with read bias after the set scan. The GNPs was aligned with 400 nm pitch. Four conductive spots shows ON state.



Fig. 5 Cross-sectional TEM image of GNP embedded NiO-GNP/Pt structure before top electrode formation. Schematic image of cross-section of the device with the grain structure. Many grain boundaries were formed above the GNPs in the NiO layer.





Fig. 6 Typical *I-V* characteristics of the GNPs embedded ReRAM and without GNPs. Dashed lines shows forming process.

Fig. 7 The differential resistance $\Delta LogI$ / $\Delta LogV$ plot against voltage during the forming process. The curvature of the *Log-Log* plot increases differently in the high-voltage region (> 2.0 V).

(a) Pt/NiO/Pt: w/o GNP



Fig. 8 Schematic image of the filament formation model NiO film in (a) Pt/NiO/Pt structure and (b) GNP embedded structure.