Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp931-932

Floating Gate Memory with High-density Nanodot Array Formed Utilizing Ti-binding Dps

Hiroki Kamitake[1,2], Kosuke Ohara[1], Mutsunori Uenuma[1,2], Bin Zheng[1,2], Yasuaki Ishikawa[1,2], Ichiro Yamashita[1,2,3], and Yukiharu Uraoka[1,2]

1 Nara Institute of Science and Technology, 8916-5 Takayamacho, Ikoma, Nara 630-0192, Japan
2 CREST, JST, 7 Goban, Chiyoda, Tokyo, 102-0075, Japan
3 ATRL, Panasonic Corporation, 3-4 Hikaridai, Seika, Kyoto, 619-0237, Japan
Tel: + 81-(743)-72-6064, Fax: + 81-(743)-72-6069 (e-mail:k-hiroki@ms.naist.jp)

1. Introduction

Nanodot-type floating gate memory (NFGM), which has a two dimensional array of nanodots as a floating gate, has the merits of high durability against charge leakage, because a nanodot independently stores charges [1]. Our group has researched to develop new functional semiconductor devices by Bio-nano process (BNP) which is one of bottom-up processes [2,3], and fabricated NFGM utilizing cage-shaped protein, ferritin which is a 12 nm cage-shaped protein with a 7 nm cavity [3,4]. Various types of the inorganic homogeneous nanometer-sized particles (bio-nanodots: BND) can be formed in its cavity by biomineralization [2]. We proposed the NFGM with a high-density nanodot-array utilizing *Listeria* Dps which is a 9.4 nm cage-shaped protein with a 4.5 nm cavity [3]. The high-performance NFGM with a high-density nanodot array can be fabricated utilizing *Listeria* Dps by suppressing the effect of the SiO_2 / Si interface states owing to increase the charge injection to floating gate. In this study, we attempted to fabricate metal-oxide-semiconductor (MOS) capacitor with the high-density Co-BND array formed utilizing *Listeria* Dps modified Ti-binding peptides on the surface, so-called Ti-binding Dps (TD) [4,5]. In addition, we compared the *C-V* characteristics of the fabricated MOS capacitor with that of the MOS capacitor with Co-BND array formed utilizing Ti-binding ferritin (TBF) [5].

2. Characterization of nanoparticle

Ferritin and *Listeria* Dps are shown in figure 1 respectively. The Co-BND appears as spherical black dot in the TEM image surrounded by a stained protein. Figure 2 shows the TEM image of Co-BNDs accommodated in TD.

After the solution of TD was concentrated by centrifugation and TD was dried in a N_2 ambient, we measured a XRD pattern of Co-BNDs in the cavity of TD (Figure 3). This result indicates that the crystal structure of Co-BND is Co_3O_4. Figure 4(a) shows the SEM image of Co-BND array formed utilizing TD. Co-BNDs were evenly distributed on SiO_2 surface after UV/ozone treatment. The adsorption density of Co-BND array formed utilizing TD was 1.3×10^{12} cm^{-2}, which is higher than that of Co-BND array formed TBF as shown in Fig. 4(b).

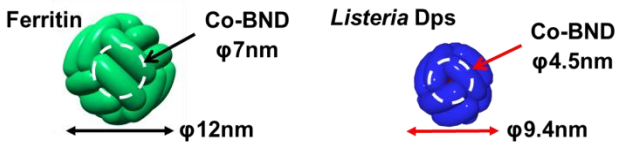

Fig.1 Ferritin and *Listeria* Dps.

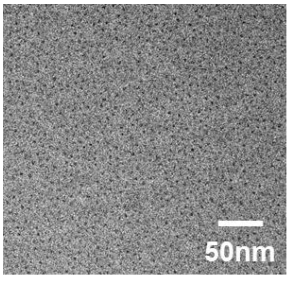

Fig. 2 TEM image of TD.

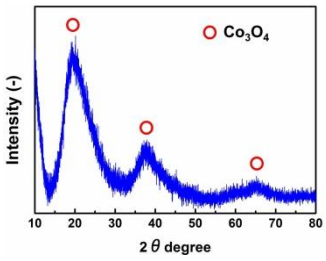

Fig.3 XRD spectrum of Co-BND.

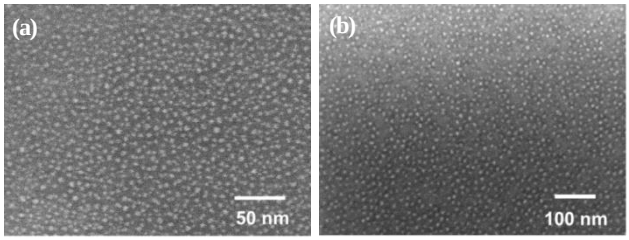

Fig.4 SEM images of Co-BND arrays formed utilizing (a) TD and (b) TBF.

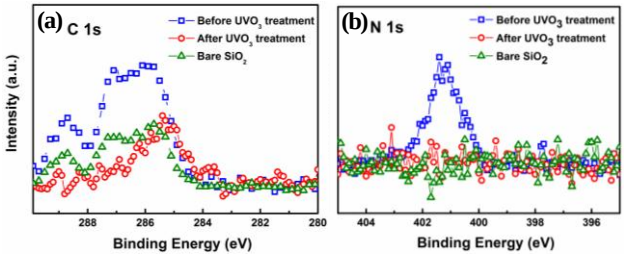

Fig.5 XPS spectrums of (a) C and (b) N before and after eliminating protein by UV/ozone treatment.

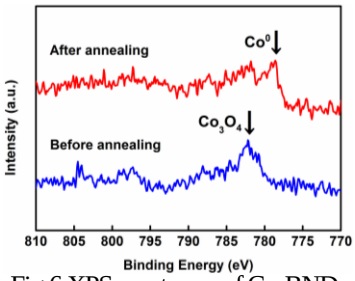

Fig.6 XPS spectrums of Co-BND after annealing in the reductive gas.

Figure 5 (a) and (b) represent the X-ray photoelectron spectroscopy (XPS) spectrums of carbon (C) 1s orbital and nitrogen (N) 1s orbital respectively. The peaks of the C and N disappeared after UV/ozone treatment. Figure 5 showed that the protein has been completely removed by UV/ozone treatment.

We also measured XPS spectrums of the Co-BNDs embedded in a 3 nm-SiO_2 to evaluate the reduction of Co-BNDs. Figure 6 shows the XPS spectrums of Co-BNDs before and after annealing in the reductive gas. The peaks of cobalt oxide appeared despite annealing. However, in the case of the samples annealed in the reductive gas, a broad peak of metallic Co was appeared. These results suggest that the Co-BND was partially reduced by annealing in the reductive gas.

3. Fabrication Process

We cleaned a Si substrate with a 3 nm-SiO_2 layer formed by rapid thermal annealing (RTA). Solution contained TD was dropped on the SiO_2 to adsorb TD on the SiO_2 and the substrate was spin-dried at 6000 rpm for 1 min. Outer proteins of TD was eliminated by UV irradiation in an ozone atmosphere for 60 min (UV/ozone treatment), to form Co-BND array on the SiO_2. After the elimination of protein, a 15 nm-SiO_2 control oxide was deposited by plasma-enhanced CVD. Following the formation of Pt/TiN top electrode and Al bottom electrode by electron beam evaporation, the fabricated MOS capacitor was annealed in a reductive gas (N_2:H_2=9:1) at 450 °C to reduce the Co-BNDs from metal oxide nanodots to metal nanodots. Figure 7 shows the device structure of MOS capacitor embedded Co-BNDs. The band diagram of the devices was deduced as shown Fig. 8.

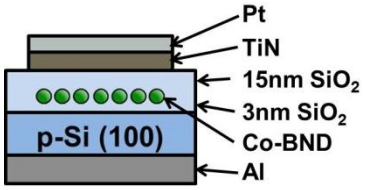

Fig.7 Schematic illustration of MOS capacitor structure.

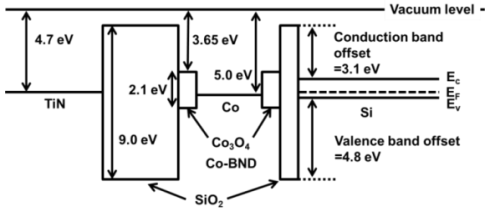

Fig.8 Band diagram of the MOS Capacitor fabricated utilizing TD.

4. Results

The *C-V* characteristics and memory windows of the fabricated MOS capacitors with Co-BND array formed utilizing TBF or TD are shown in Figure 9 and 10. The result of MOS capacitor without Co-BND indicates that the protein was completely removed by UV/ozone treatment without influencing the device operation. When a voltage is applied to the MOS capacitor with Co-BND, a hysteresis caused by charge injection into Co-BND was observed. The hysteresis of the MOS capacitor formed utilizing TD was larger than that of the MOS capacitor formed utilizing TBF. The enlargement of hysteresis was caused by increasing the amount of charge injected into Co-BND array because the adsorption density of Co-BND increased by utilizing TD.

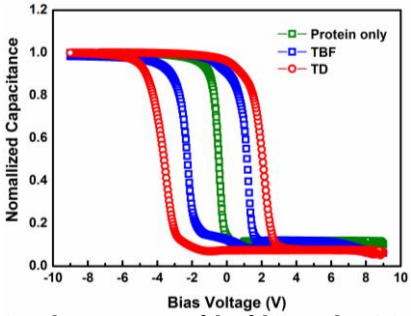

Fig.9 *C-V* characteristics of the fabricated MOS capacitors.

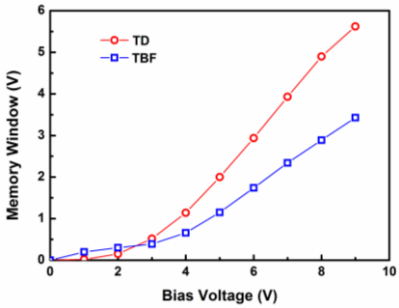

Fig.10 Memory windows of the fabricated MOS capacitors.

5. Conclusion

We increased the adsorption density of Co-BND array over 10^{12} cm^{-2} by utilizing TD. The XRD pattern indicated that the crystal structure of Co-BND is Co_3O_4. In addition, the *C-V* characteristics of MOS capacitor and the measurement results of the XPS spectrums of C 1s and N 1s showed that the protein of TD was completely removed by UV/ozone treatment without influencing the device operation. The hysteresis of the MOS capacitor fabricated utilizing TD was larger than that of the MOS capacitor fabricated utilizing TBF. We confirmed that the high-performance memory can be fabricated utilizing TD, compared with utilizing TBF. These results contribute to realizing a next-generation memory.

6. Reference

[1] S. Tiwari *et la.*, *Appl. Phys. Lett.* 68, 1377 - 1379, (1996).
[2] K. Ohara *et al.*, *Appl. Phys. Express*, 2, 9 (2009).
[3] K. Yamada *et al.*, *J. Appl. Phys*. 45, 11 (2006).
[4] T. Hayashi *et al.*, *Langmuir*, 25, 18, 10901-10906, (2009).
[5] T. Hashimoto *et al.*, *J. Appl. Phys*. 99, 263701 (2011)