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Controlled reduction of BioNanoDots for Better Charge Storage Characteristics of BND Flash Memory

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1. Introduction

Recently decent attention has been focused on semiconductor nanodot embedded metal-oxide-semiconductor (MOS) memory device for future high speed and low pow -er consuming logic and memory devices. Conventional flash memory uses a plate-type floating gate for electric charge storage node. Utilization of the nanodot as a floating gate is promising approach to improve device property of flash memory. We have been demonstrating BioNanoDot (BND) utilization as the electric charge storage node of flash memory[1,2]. We call this biomolecule utilized device fabrication as BioNanoProcess (BNP). The BNDs are synthesized as metal oxide due to the synthetic process in aqueous solution, therefore reduction of synthesized BNDs is necessary for improvement of charge storage characteristics of BND utilized flash memory devices. We have reported that the reduction of iron oxide BNDs (Fe-BNDs) can be achieved by annealing of embedded Fe-BNDs [3]. It is considered that the conversion of oxide BND to metal BND by reduction treatment will improve the charge storage capability of oxide BND utilized flash memory. In this contribution, we report the controlled reduction of cobalt oxide BND (Co-BND) by changing the reduction conditions, such as atmosphere and temperature. Observed memory characteristics of Co-BND flash memory fabricated with different annealing conditions suggest that reduction condition dependence of charge storage characteristics and improvement of charge storage capacity of Co-BND memory.

2. Experimental details

Figure 1 depicts a schematic drawing of ferritin (left) and the cross-section of Co-BND accommodated ferritin (right). Ferritin gives several advantages for flash memory fabrication process such as, 1) Uniform BNDs (Approximately 7nm) can be synthesized by using cage-shaped ferritin protein as templates. 2) High density and selective deposition is possible due to the self assemble ability of protein outer surface. 3) Different kinds of metal or semiconductor nanodots can be incorporated by replacing Fe. The BNDs, used as charge storage node of memory, were synthesized in the vacant cavity of ferritin protein by biomineralization [2].

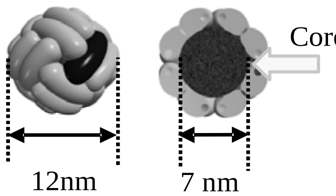

Fig. 1. Ferritin protein involving inorganic material.

Co-BND accommodated ferritins were adsorbed on p-Si substrates with 3-nm-thick thermal oxide thin film. To prevent the multilayer formation, drop cast of ferritin solution was spin out in a sealed plastic tube. Outer protein shell was removed by oxidation by UV irradiation under ozone atmosphere, and obtained Co-BND array. To prevent the re-oxidation of annealed Co-BNDs and achieve the controlled reduction of Co-BNDs, fabricated Co-BND array was buried in thin SiO_2 film. The thickness of SiO_2 was set to 5 nm for X-ray photoelectron spectroscopy (XPS) measurements. Annealing of fabricated samples were carried out under inert (N_2, 100%) and reductive (H_2:N_2=4%:96%) atmosphere. Samples were annealed at 350, 450, 600, 700, 800°C for 10min. Annealed samples were measured by XPS and transmission electron microscopy (TEM) to confirm the reduction of embedded Co-BNDs and the morphology after high temperature annealing.

We also fabricated annealed-Co-BND embedded MOS capacitor and measured high-frequency capacitance-voltage (C-V) characteristics to study the effect of the reduction

2. Result and discussion

Composition estimation

As we described, synthesized BND in protein shell was synthesized as cobalt oxide, Co_3O_4. XPS spectra of Co-BND after annealing under inert, 100% of N_2, (Fig.2, left) and reduction, 4% of H_2, (Fig. 2, right) atmosphere are shown. It is reported that Co_3O_4 has Co $2p_{3/2}$ signal at 779.5 eV [2]. As we can see in XPS spectra of N_2 annealed samples, Co $2p_{3/2}$ peak was observed for all anneal temperature. In contrast to N_2 anneal, XPS spectra of H_2 annealed samples show emerge of new peak at 778.3 eV. This peak is assigned to $2p_{3/2}$ of metal Co. In H_2 atmosphere, metallic Co peak appeared from 350°C and only metallic Co peak was observed at 800°C. These results indicated that annealing atmosphere is more important than annealing temperature for controlled reduction of embedded BNDs. Peak intensity change after H_2 anneal suggest that control of reduction ratio between Co_3O_4 and metal Co is possible by choosing appropriate temperature for anneal. Most of the embedded oxide-Co-BND was reduced to metal-Co-BND over 450°C. This suggest that we can expect good charge storage capability based on the metal charge storage node of flash memory.

Morphology estimation

From the view point of the use of annealed-BNDs for flash memory, the morphology of BNDs after high temperature treatment should be confirmed. Figure 3 depicts cross-sectional TEM image of embedded Co-BNDs before (left) and after (right) annealing under reductive atmosphere at 350°C, 450°C, 600°C, 700°C, 800°C.

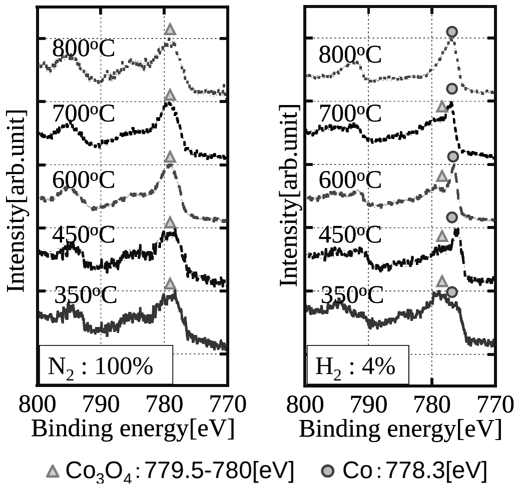

Fig. 2 XPS spectrum of samples in different anneal atmosphere

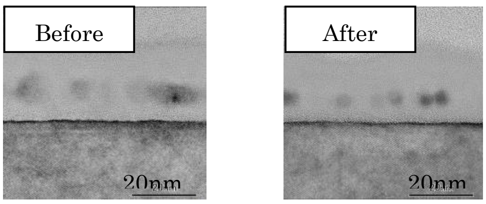

Fig. 3 TEM images of Co-BNDs before and after annealing in the reduction atmosphere.

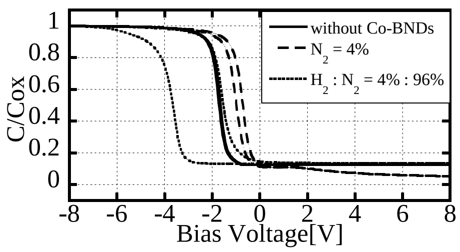

Fig. 4 C-V characteristics (a) without Co-BNDs, (b) 800°C annealing under inert atmosphere, (c) 800°C annealing under reductive atmosphere

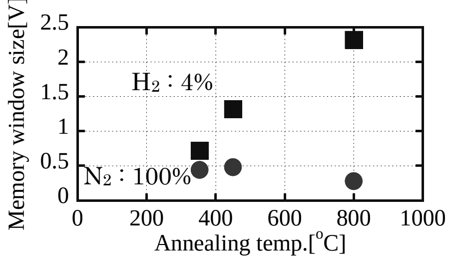

Fig. 5 Memory window size- Annealing temp. characteristics

Because high-temperature treatment in the case of the sample annealed before and after, to examine the morphology of the reduced nanodots in SiO_2, TEM analysis were performed for non-anneal and annealed sample as shown in Fig. 3. As seen in the figures, embedded BNDs kept their spherical shape even after anneaing. This result suggests that the Co-BNDs embedded in SiO_2 are strong against heat treatment. From the detailed analysis of TEM image suggest slight change of the size after anneal. This is due to the desorption of oxygen from the BND.

C-V characteristics

Figure 4 shows observed C-V characteristics of fabricated Co-BND embedded MOS Capacitors. Curve (a), (b) and (c) in Fig. 4 depicts the C-V obtained with (a) reference without BND, (b) annealed in N_2 at 800°C and (c) annealed in H_2 at 800°C, respectively. In the case of capacitors without BND (a), no hysteresis was observed. Meanwhile, we observed anti-clockwise hysteresis due to the charge injection to the embedded Co-BND in (b) and (c).

Memory window was examined by Capacitance - Voltage curve as shown in Fig.4. Hysteresis was observed in the capacitors with core (b). Furthermore, larger memory windows were observed under reduction atmosphere (c).

Relationship between annealing temperature and observed memory window size (ΔV) is summarized in Fig. 5. N_2 annealed samples (depicted with circle) showed similar ΔV independent to the anneal temperature. Instead, the ΔV of H2 annealed MOS capacitors increased by the increase of anneal temperature. Based on the spectral change in XPS, observed widening of memory window is considered due to the increment of metallic portion of Co-BND. This result suggest that the reduction of oxide-Co-BND to metal-Co-BND can improve charge storage capacity of BND utilized flash memory.

3. Conclusions

We demonstrated controlled reduced of Co-BNDs synthesized in ferritin protein for the application to floating gate memory. We investigated the morphology, composition and memory window sizes after anneal. We confirmed that Co-BNDs were reduced to metallic-Co-BND under H_2 atmosphere at relatively low temperature (~450 °C) without collapsing and changing its morphology. We also observed that metallic Co-BND strongly contributed to the charge storage capacitance increase.

Acknowledgements

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