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Reduction of a Ferritin Core Embedded in Silicon Oxide Film for An Application to Floating Gate Memory

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1. Introduction

We have proposed a new process technology, termed "bio-nano-process", that combines semiconductor processing technology and bio-technology[1]. We have already demonstrated the effectiveness of this new technology by replacing a ferritin protein iron core with a cobalt core using biomineralization technology[2]. We utilized the core as an electronic node, and succeeded in performing the operation of floating gate memory with it. In order to extend the application of this technology further, we propose a new method which uses the iron core present in a ferritin protein as an electronic node. As shown in Fig. 1, the ferritin core is a hydratated form of electrically insulating ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$). Therefore, in order to utilize the core as an effective charge storage node for memory, it is necessary to reduce the core to make it electrically conductive.

In this study, we attempted to reduce the ferritin core embedding in silicon oxide film by annealing in hydrogen.

2. Experimental

To reduce a ferritin iron oxide core embedded in a SiO_2 film, we carried out heat treatment in hydrogen atmosphere. The detailed experimental method is described below.

A heat oxide film with a thickness of 3 nm was synthesized on a p-type silicon substrate, and Fe ferritin was made to adsorb onto the substrate. Then, the outer protein of Fe ferritin was removed by UV ozone treatment at 115°C for 40 min. A 5-nm-thick SiO_2 thin film was deposited at 300°C by plasma CVD using tetraethoxysilane (TEOS)/O_2 gas. After the deposition, rapid thermal annealing (RTA) was carried out in hydrogen atmosphere using a lamp furnace.

To examine the temperature dependence of the reduction reaction response, the heat treatment was carried out up to 900°C. Because XPS was used in determining the elemental composition of the Fe core after the reduction, the thickness of the SiO_2 deposited was maintained at 5 nm or less.

3. Results and Discussion

Figure 2 shows an XPS profile of the region of Fe2p, in which the dependence of the responsiveness of heat treatment on temperature in the range from 200°C to 900°C was measured through heat treatment in hydrogen atmosphere. Each spectrum was corrected using the peak of C1s (284.5 eV).

First, an Fe peak at approximately 706.5 eV appeared at 400°C. Fe peak intensity increased with increasing heat-treatment temperature. At 900°C, the spectral shape of only Fe was observed, indicating that the iron oxide core was reduced and Fe dots were formed in the oxide film. Focusing on the Fe_2O_3 peak, the peak position, which was 711 eV before the heat treatment, shifted to approximately 710 eV after the heat treatment at 300°C. This result indicates the existence of Fe_3O_4 (magnetite: 710 eV), which is a complex of Fe^{2+} and Fe^{3+}. With further increase in temperature, the peak position shifted to the lower restraining-energy side, suggesting the existence of FeO (usutite: Fe^{2+}, 709.5 eV).[4] According to the Ellingham diagram, iron oxide is difficult to reduce in the order of Fe_2O_3, Fe_3O_4, and FeO.[5] Therefore, it is considered that Fe_2O_3 was reduced to Fe via reduction intermediates such as Fe_3O_4 and FeO. Therefore, the change in the existence ratio of these reduction intermediates in the core, which is due to the reduction during the heat treatment, affects the peak shift of Fe_2O_3.[6]

Figure 3 shows the XPS profile of the O1s region. The peak corresponding to Fe_2O_3 (approximately 529.5 eV), which was seen before the heat treatment, decreased in intensity after the heat treatment. This also indicates the reduction of the ferritin core. In addition, the core was not reoxidized when the sample was exposed to air after the reduction, indicating that when Fe ferritin is embedded in SiO_2, the SiO_2 film functions as a reoxidation-preventing film.

Figure 4 shows a cross-sectional TEM image of the sample in which Fe ferritin cores were embedded within the SiO_2 film and heat-treated at 800°C for 5 min in hydrogen atmosphere. The Fe ferritin cores are shown as black dots surrounded by the brighter SiO_2 in the

image. The unchanged shape of the cores after the heat treatment indicates that their aggregation due to the high-temperature heat treatment can be prevented by embedding the Fe ferritin cores in SiO_2. This is because SiO_2 prevents the diffusion of Fe atoms by acting as a blocking layer for Fe-atom diffusion.

Figure 5 shows an enlarged TEM image of the area around a dot. Distinctive lattice patterns are identified on the Si substrate and dot. Because an electron beam is incident in the [110] direction against the Si substrate, the lattice pattern on the Si substrate appears on the {111} facet and the lattice spacing is 0.313 nm. Here, the diameter of the dot and the lattice spacing can be accurately measured. Lattice patterns with a spacing of approximately 2.0 nm are observed in two directions on the dot. These correspond to the lattice patterns observed when the electron beam is incident in αFe in the [100] direction. Considering the XPS profile, the dot is considered to correspond to monocrystalline Fe. The size of the dot was measured to be approximately 5.1 nm. Because the diameter of the ferritin iron oxide core before the reduction was approximately 7 nm, oxygen atoms were thought to have desorbed during the reduction, which diminished core diameter.

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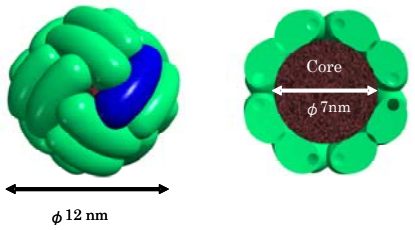

Fig.1 The schematic drawing of ferritin molecule.

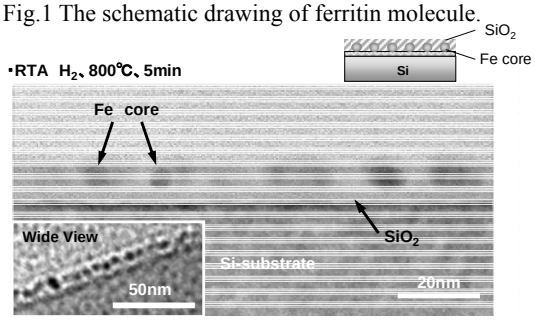

Fig.4 Cross-sectional TEM image of the sample in which Fe ferritin cores were embedded within the SiO_2 film.

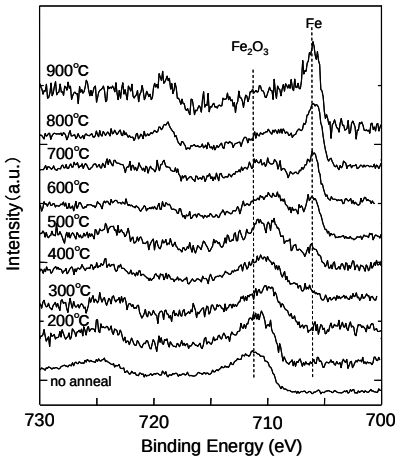

Fig.2 XPS profile of Fe2p signal measured trough heat treatment in the range from 200°C to 900°C in hydrogen atmosphere. Each spectrum was corrected using the peak of C1s (284.5 eV).

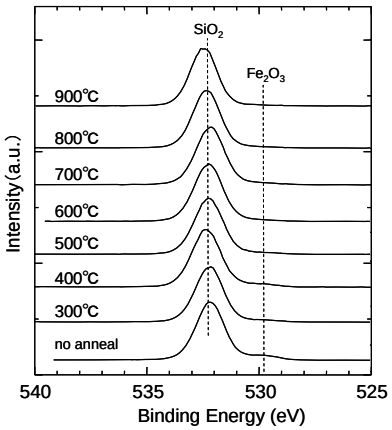

Fig.3 XPS profile of the O1s region. The peak corresponding to Fe_2O_3 (approximately 529.5 eV), which was seen before the heat treatment, decreased in intensity after the heat treatment.

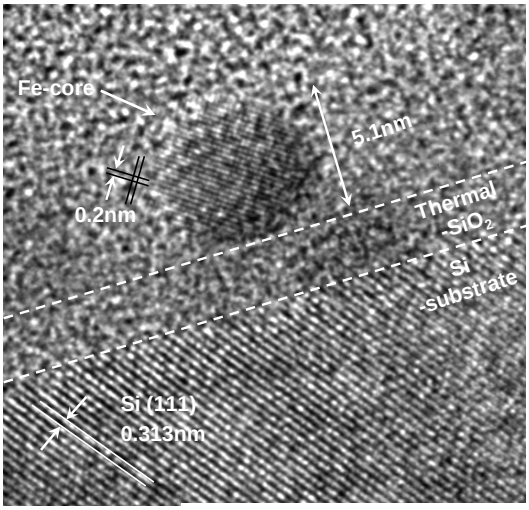

Fig.5 Enlarged TEM image of the area around a dot. Distinctive lattice patterns are identified on the Si substrate and dot.