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High-Density Floating Nanodots Memory Produced by Cage-Shaped Protein

Kiyohito Yamada[1], Shigeo Yoshii[1], Shinya Kumagai[1], Atsushi Miura[2], Yukiharu Uraoka[2], Takashi Fuyuki[2] and Ichiro Yamashita[1, 2, 3]

[1]Advanced Technology Research Laboratories, Matsushita Electric Industrial Co., Ltd.,
3-4 Hikaridai, Seika, Kyoto 619-0237, Japan
Phone: +81-774-98-2516 E-mail:yamashita.ichiro@jp.panasonic.com
[2]Graduate School of Materials Science, Nara Institute of Science and Technology,
8916-5 Takayama, Ikoma, Nara 630-0101, Japan
[3]Core Research for Evolutional Science and Technology, Japan Science and Technology Agency,
4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

1. Introduction

Nanotechnology is attracting a great deal of researcher's attention and nanofabrication is one of the hottest topics in the nanotechnology. We propose a new biological method which can produce nanometric inorganic functional structures utilizing biomineralization, self-assembly and vulnerability of the protein supramolecules. This method was named "Bio Nano Process" (BNP).[1-4)]

As the first application of the BNP, we have been producing an array of nanodots embedded in the SiO_2 layer of the metal-oxide-semiconductor (MOS) capacitor, which is the key component of the floating gate memory MOS transistor. In this paper, we described the each step of the fabrication of the MOS capacitor with nanodots array produced by a small cage-shaped protein, *Listeria* ferritin (Lis-fer) with 4.5nm ferrihydrite core. The density of nanodots array produced by Lis-fer should exceed 10^{12} cm^{-2}, [4)] which is desirable to suppress the effect of interface trap density at SiO_2/Si. We also described the electric properties of the fabricated MOS.

2. Experimental

A p-type Si substrate with a 3 nm thick SiO_2 layer was exposed to 3-aminopropyl-triethoxysilane (APTES) vapor and SiO_2 surface was covered with APTES.

Lis-fer with ferrihydrite core was adsorbed on the APTES modified Si substrates. The adsorption density of Lis-fer was observed by a high resolution scanning electron microscope (HR-SEM).

Then, the protein shells and APTES layer were eliminated by heat- or UV/ozone treatment and an array of nanodots was obtained. The traces of carbon and nitrogen atoms on the surface were examined by an X-ray photoelectron spectrometer (XPS).

After the protein and APTES elimination, a SiO_2 layer with a thickness of 20 nm was deposited on the substrate with an array of ferrihydrite cores by PECVD method using tetraethyl-orthosilicate (TEOS) as silicon source and Al electrode was deposited on the SiO_2. The obtained MOS structure was annealed at 450°C for 1h in reducing ambient gas (H_2 : N_2 = 10% : 90%). Capacitance-voltage characteristics of the MOS capacitor were measured.

3. Results and Discussion

Fig. 1 shows the SEM image of the substrate after Lis-fer adsorption. Since SEM can not visualize protein shells, only nanodot cores can be seen as white dots. The density of nanodots was 1.8 x 10^{12} cm^{-2}, which is higher than the target density 10^{12} cm^{-2}.

We attempted two methods for the selective elimination of protein shell, heat- and UV/ozone treatments. In the case of the UV/ozone treatment, aggregates of nanodot cores were observed. (Fig.2a). To avoid this aggregates we conducted heat-treatment at 500°C for 10min by a rapid thermal annealing (RTA), which was proven to eliminate protein completely by XPS (Fig. 3). Cores did not make aggregates. (Fig. 2 b) This difference may come from the way of protein elimination. The energy of UV light is high enough to cut the chemical bonds of protein and the stable protein scaffold which maintains Lis-fer monolayer array structure was destroyed. Therefore, cores moved freely and aggregated. On the other hand, the heat-treatment made the protein shell into carbonaceous state which formed stable matrix. Cores were buried in the matrix and they were fixed during protein oxidation. Therefore independent nanodots cores were distributed evenly. Judging from these results we employed the heat-treatment for the protein elimination.

The protein elimination was confirmed by XPS measurements. Fig 3 shows the results. N1s signal completely disappeared after heat-treatment and C1s signal became the same level before the heat-treatment.

Capacitance-voltage (C-V) characteristics of the MOS capacitor were measured to investigate electron confinement in the nanodots. Fig. 4 (a) shows the result and there is a clear hysteresis. The anti-clockwise hysteresis can be observed reproducibly, and it indicated the charging and discharging of electron in the embedded Lis-fer cores. C-V curve of the same MOS capacitor but produced using Lis-apofer, which consists of only protein shell without core, did not show any hysteresis as shown in Fig. 4 (b). The flat band shift was larger than our previous work, which employed ferritin molecule as cage-shaped protein.[3)] These results clearly indicate that the electrons are confined within the array of high density nanodots made by Lis-fer.

4. Conclusions

High-density (1.8 x 10^{12}cm^{-2}) Lis-fers with homogenous ferrihydrite core were adsorbed onto the APTES modified Si substrate. The protein shells and APTES layer were eliminated by heat treatment and the obtained array of cores were embedded in SiO_2 layer. The MOS capacitor with nanodots showed hysteresis in CV curve, which indicates the electron confinement in the cores made by Lis-fer. The results described in this paper clearly demonstrated that Lis-fer will make it possible to fabricate much scaled floating gate type memory.

Acknowledgements

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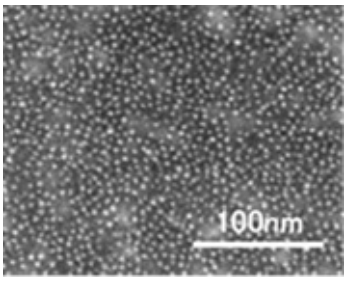

Fig. 1 SEM image of Lis-fer molecules adsorbed onto substrate modified by APTES. The density of Lis-fer was approximately 1.8 x 10^{12} cm^{-2}.

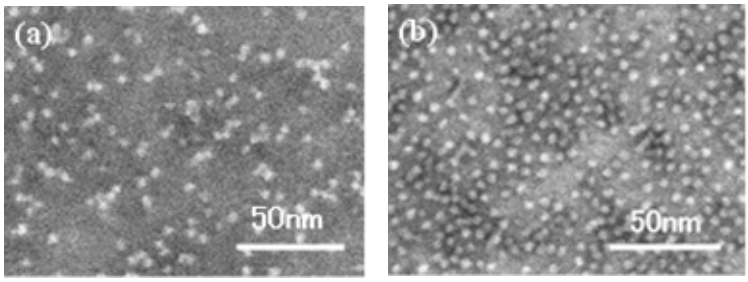

Fig. 2 SEM image of Lis-fer core array onto substrate after the outer protein shell and APTES layer were removed by (a) UV/ozone treatment and (b) heat-treatment. (a) Aggregates of the cores were seen. (b) Independent cores were seen.

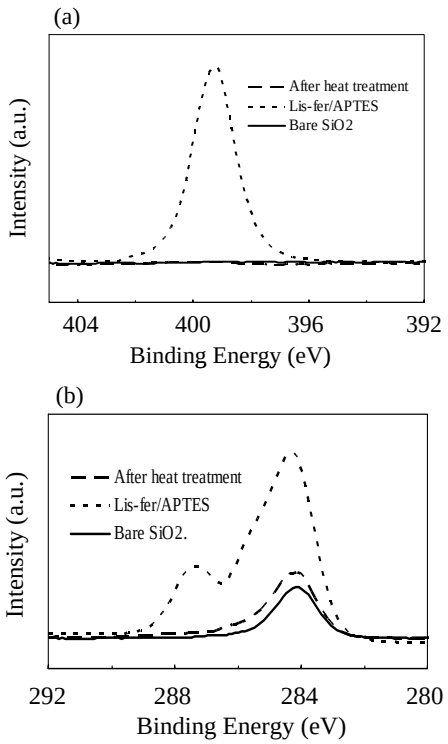

Fig. 3 XPS signals of (a) N1s and (b) C1s from the silicon substrate with Lis-fer array before and after heat treatment under oxygen gas. The broken lines correspond to the sample after 500^{o}C heat treatment under oxygen gas, the dotted lines correspond to the sample with APTES and Lis-fer layer and the solid lines correspond to bare silicon dioxide.

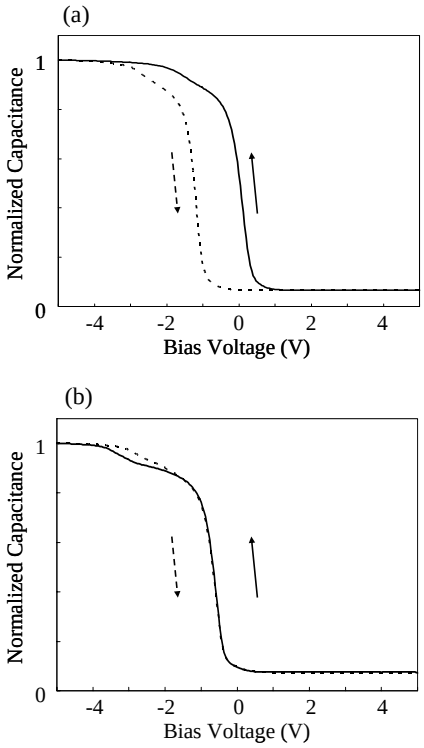

Fig. 4 Capacitance-voltage characteristic of MOS structure (a) with and (b) without iron nanodots. In the capacitance with the iron nanodots made by Lis-fer, the hysteresis was clearly observed.