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Floating Gate MOS Capacitor with High-Density Nanodots Array Produced by Protein Supramolecule

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1. Introduction

Nanotechnology is attracting a great deal of research 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. This method named "Bio Nano Process" (BNP) utilizes biomineralization, self-assembly and vulnerability of the protein supramolecules.[1-6)] As the first application of the BNP, we have been producing a monolayer of nanodots embedded in the SiO_2 layer of the MOS capacitor, which is the key component of the floating gate memory MOS transistor (FNGM).[3)] In order to realize sufficient magnitude and uniformity for the memory window and decrease the influence of interface traps in SiO_2/Si on the memory window, a nanodot density of higher than 10^{12} cm^{-2} is necessary. Therefore, we employed small cage-shaped protein with ferrihydrite core, *Listeria* ferritin (Lis-fer), the outer and inner diameters of which are 9.4 and 4.5 nm, respectively. The density of a nanodot array produced using Lis-fer should exceed 10^{12} cm^{-2}.[4, 6)]

In this paper, we present each step of the fabrication of the MOS capacitor with a 4.5-nm-nanodot array using Lis-fer and the electrical properties of the obtained MOS capacitor.

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 was adsorbed on the APTES modified Si substrates by controlling the electrostatic interaction between the protein and the substrate surface.[4)] The adsorption density of Lis-fer was observed by a high resolution scanning electron microscope (SEM). After the protein shell and APTES elimination, a SiO_2 layer with a thickness of 20 nm was deposited on the substrate with an array of nanodots 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^{o}C for 1h in reducing ambient gas (H_2:N_2=10%:90%). To investigate the geometric condition and the elements of nanodots in the SiO_2 layer after annealing, a cross-sectional transmission electron microscope (TEM), an X-ray photoelectron spectrometer (XPS) and electron-energy-loss spectroscopy (EELS) was carried out. Capacitance-voltage (C-V) 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}. Since the ferrihydrite core of Lis-fer is nonconductive, the core needs to be reduced to the conductive nanodot for electron confinement. Therefore, the reduction process of the obtained MOS structure was employed by annealing.

The geometric conditions of the embedded nanodots and MOS structure were investigated by cross-sectional TEM. As shown in the TEM image (Fig. 2), the Lis-fer nanodots embedded in a SiO_2 layer after annealing were just above the tunnel oxide layer and have a spherical shape. And the diameter of the Lis-fer core decreased from 4.5 to 3.2 nm after annealing. This shrinkage also supports the desorption of oxygen atoms from a ferrihydrite core during annealing. They are isolated from other nanodots, which is important for the floating nanodot gate memory or electron confinement nodes.

The XPS, Fe 2p, spectrum of nanodot embedded in SiO_2 layer was measured before and after annealing, as shown in Fig. 3(a). The XPS spectrum showed a peak corresponding to Fe_2O_3 at 711 eV before annealing. After annealing, a new peak at 707 eV corresponding to metal iron appeared and a broadening toward the low energy side of the peak around 711 eV could be attributed to FeO, which has a peak at 710 eV. That is, cores embedded in the 5-nm-thick SiO_2 layer used in XPS were reduced partially from Fe_2O_3 to Fe_3O_4, FeO or Fe. To investigate the elements of nanodots in SiO_2 after annealing, EELS measurement was carried out. Fig. 3(b) shows the EELS signals corresponding to O-K obtained from a nanodot. The typical peak shape of an iron oxide was not observed after annealing.[3)] From results of the above cross-sectional TEM, XPS and EELS observation, we suppose that the an iron oxide core reduced to a metal iron after annealing, which is supported by our previous work.[3)]

The C-V characteristics of the MOS capacitor measured at 1 MHz with DC sweep of ±10V showed a clear hysteresis, as shown in Fig. 4. The anti-clockwise hysteresis can be observed reproducibly, and it indicated the charging and discharging of electron in the embedded nanodots. The flat band shift (ΔV_{fb}) as the capacitance hysteresis is plotted against dot density in Fig. 5. This result indicated that ΔV_{fb} increases with increasing dot density and expanded ΔV_{fb} will enhance device performance when applied in floating nanodot memories.

By using BNP, nanodots array controlled dot size and density and selected dot type can be fabricated on substrates.[1,4,5] Therefore, it is possible to investigate effects of dot size, dot density and dot type on charge injection characteristics in nanodots array and we expect to obtain knowledge to improve FNGM in the future.

4. Conclusions

High-density Lis-fers above 10^{12}cm^{-2} with a ferrihydrite core were adsorbed onto a Si substrate. The protein shells were eliminated by heat treatment and the obtained array of cores was embedded in a SiO_2 layer. After forming an aluminum electrode on this SiO_2 layer, the sample was annealed in reducing gas. 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 study clearly demonstrate that a larger memory window, or ΔV_{fb}, can be attained by employing an array of high-density nanodots, which will make it possible to fabricate much scaled floating gate type memory.

Acknowledgements

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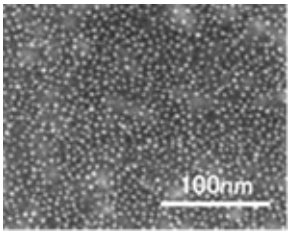

Fig. 1 SEM image of Lis-fer molecules adsorbed onto substrate modified by APTES. The density of Lis-fer was approximately 1.8 x 10^{12} cm^{-2}.

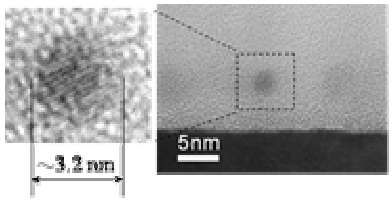

Fig. 2. Cross-sectional TEM image of cores embedded in SiO_2 after annealing. The nanodots are independent and the diameter of a nanodot is 3.2 nm.

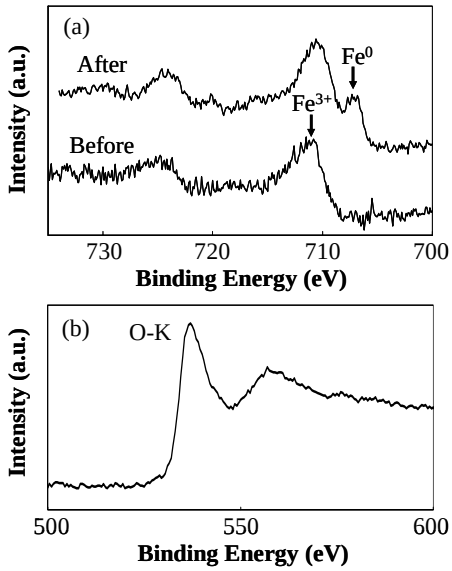

Fig. 3. (a)XPS, Fe2p spectrum of core embedded in 5-nm-thick SiO_2 layer observed before and after annealing. (b)EELS spectrum obtained from nanodot embedded in SiO_2 after annealing in reducing gas.

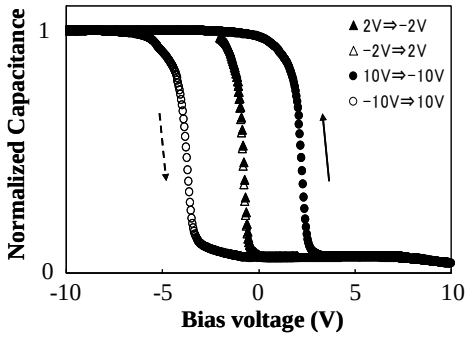

Fig. 4. C-V characteristics of MOS structure with nanodots. In the capacitance of the structure with the nanodots produced by Lis-fer, the hysteresis was clearly observed.

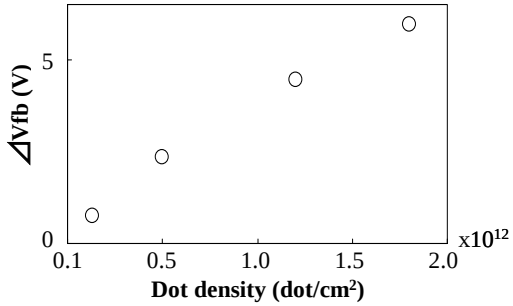

Fig. 5. Flat band shift (ΔVfb) increased with dot density increasing.