Electrical Characteristics of ferritin cores Investigated by Kelvin Probe Force Microscopy

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Abstract We fabricated Fe (iron metal) cores structure by using a low energy Ar+ ion beam. A monolayer of ferritin molecule (Fe₂O₃: iron oxide) was adsorbed on the thermal silicon oxide layer. The bombardment energy was optimized using Ar gas by changing the input power after the protein of the monolayer was eliminated with UV/O3. Though it was resulted in a poor reduction when the time of ion beam was less than 30 sec, Ar+ ion beam enabled completely reduction when the time of ion beam was in 60 sec. We reduced the core particles to conductive Fe nanodots. X-ray photoelectron spectroscopy (XPS) measurements confirmed the reduction of the cores. As a result, the diameter of the ferritin nano-structure was 7 nm, which was not identical to that of the iron core in the ferritin after ion beam. Additionally, the Kelvin Probe Force microscopy (KFM) profile was not almost identical between Fe₂O₃ and Fe cores. It is very difficult for conventional Ar+ beam processes to fabricate such fine structure of Fe cores, because the high energy ions enhanced the bombardment damage of the iron core in the conventional reduction processes. The results that the change of lattice constant from 0.25 to 0.2 nm corresponds from ferrihydrite (110) to α-Fe(111), respectively, which suggests the ferrihydrate cores reduced to Fe nanodots after ion beam process. Furthermore, the diameter of the ferritin core decreased from 7 nm to 5 nm after the ion beam process.
Introduction

Surface structures and local surface potential of $\text{Fe}_2\text{O}_3$ and Fe of ferritin nanoparticle on a Si substrate were investigated by Kelvin Force microscopy (KFM) in order to study the local electrical properties at the metal cores–KFM tip. The results for $\text{Fe}_2\text{O}_3$ indicate perfectly the reduction of oxides in agreement with previously reported results [1]. We prepared the ultrathin core films of ferritin deposited on a Si by wet process. Local surface potential of the films were mapped by Kelvin probe force microscopy (KFM), which was originally developed by Nonnenmacher et al [2]. We performed surface measurements by a KFM to find the difference in work function between $\text{Fe}_2\text{O}_3$ and Fe, which might be correspond to the particles of metal oxidation and pure metal observed by KFM. The measurements were made using the frequency modulation (FM) technique, which is used in noncontact atomic force microscopy (nc-AFM).

This new ion beam method can be used to produce a dispersed inorganic nanoparticle monolayer on a silicon substrate as designed, which could be used as a nanodot array in floating nanodot gate memories.

Experiment

1.1. Design and operating principle

In this study, we used a commercially available AFM instrument (JEOL: JSPM-4200) for KFM measurements. Since surface potential is very sensitive to humidity in air,[3] KFM measurements were carried out at a pressure of $1.0 \times 10^{-3}$ Pa. For this reason, we used a frequency modulation (FM) detection method [4]. Figure 1 shows a schematic diagram of the KFM setup. The original frequency shift detector was replaced with a newly developed one (Kyoto Instruments: KI- -

![Fig. 1 Schematic illustration of a KFM setup using FM detection. AGC: auto gain controller, LPF: low pass filter, PLL: Phase-lock loop detector. The inset depicts a schematic representation of the ferritin protein structure.](image-url)
The typical frequency shift used in this experiment ranged from -10 to -15 Hz.
Si cantilevers coated with a Pt film were used (Olympus: AC240TM-B2). The resonant frequency was about 78 kHz and the spring constant was 2 N/m. A modulation bias voltage (2 kHz, 0.8 Vrms) for KFM measurements was applied to the sample. Fig. 1 shows the electrical connections to measure the surface potential.

3. Results

3.1 KFM Measurements of Fe₂O₃ and Fe

Figure 2 shows the topographic (a) and surface potential image (b) induced on the Fe₂O₃ nanoparticle on SiO₂/Si substrate before Ar⁺ ion bombardment. We have no contrast in an image (b) of surface potential before Ar⁺ ion bombardment because surface potential between Fe₂O₃ and SiO₂ were very similar.

When the sample is subjected to Ar⁺ ion bombardment, the induced photoelectrons in the ferritin and surface change the surface potential difference between Fe and SiO₂ by a 250 mV. Due to the finite surface, charge accumulates on top of the silicon oxide surface to attenuate or cancel such potential difference. This change is probably caused by the bombardment of Ar⁺ ions. The KFM signal depends strongly on the actual condition of the surface. Stable KFM images have been obtained at high contrast and potential between Fe and SiO₂. It is suggested that near surface Fe(+) is located in a geometrically non-equilibrated position, but moves to the equilibrated position under Ar⁺ ion bombardment in an analogous to the behaviors of Fe oxidation. This results in the generation of the difference in work function and induces the surface charges. If this phenomenon causes the change of the surface potential of Fe, it may also be the fundamental origin of the ion bombardment activity in materials with the metal-oxidation-type crystal structure. The results that the change of lattice constant from 0.25 to 0.2 nm corresponds from ferrihydrite (110) to a-Fe(111), respectively, which suggests the ferrihydrite cores reduced to Fe nanodots after ion beam process. Furthermore, the diameter of the ferritin core decreased from 7 nm to 5 nm after the ion beam process.

Fig. 2 (a) topography, (b) surface potential induced on Fe₂O₃ polycrystalline before Ar⁺ ion bombardment, (b) measured by KFM initially shows no contrast of the potential.
Fig. 3 The structure consisted of two Fe atoms surrounded by three oxygen atoms. (d) surface potential induced on Fe polycrystal by Ar\(^+\) ion beam. The profile of the surface potential measured by KFM shows an abrupt increase after bombardment.

4. Conclusions
This report, that the electron confinement in the quantum nanodots are produced using ferritin, is the convincing evidence that the biomolecule can be introduced into the fabrication process of electronic devices. The results obtained here will open up a new field combining semiconductor technology and biotechnology.

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