Compositional Changes Induced by Ion Bombardment in Ferritin nanoparticles

To cite this article: Shin-ichi Yamamoto et al 2007 J. Phys.: Conf. Ser. 61 1276

View the article online for updates and enhancements.

Related content
- Surface Potential Difference of Biominalized Inorganic Nanodot by Kelvin Probe Force Microscopy
  Shin-ichi Yamamoto, Hideki Yoshioka, Yukiharu Uraoka et al.
- Sputtering of Iron under Molecular Ion Bombardment
  D. Ghose, D. Basu and S. B. Karmohapatro
- Controlled Evolution of Silicon Nanocone Arrays Induced by Ar⁺ Sputtering at Room Temperature
  Li Qin-Tao, Li Zhi-Gang, Xie Qiao-Ling et al.

Recent citations
- Static and dynamic observation of supermolecular protein, ferritin, using high-speed atomic force microscope
  S.-I. Yamamoto et al
- Electric Properties of the Co-nanodots using Kelvin Probe Force Microscopy
  Shin-ichi Yamamoto
- Compositional Changes in Co–Ferritin Nanoparticles Induced by Ion Bombardment as Determined by Kelvin Probe Force Microscopy in High Vacuum
  Shin-ichi Yamamoto et al
Compositional Changes Induced by Ion Bombardment in Ferritin nanoparticles

Shin-ichi Yamamoto
Department of Electrical Engineering, Kobe City College of Technology, 8-3, Gakuen-higashimachi, Nishi-ku, Kobe, 651-2194, Japan

Hideki Yoshioka
Hyogo prefectural institute of technology, 3-1-12, Yukihiro-cho, Suma-ku, Kobe, 654-0037, Japan

Yukiharu Uraoka, Takashi Fuyuki
Materials Science, Nara Institute of Science and Technology, 8916-5, Takayama, Ikoma, Nara, 630-0192, Japan

Mitsuhiro Okuda, Ichiro Yamashita
Matsushita Electric Industrial Company, Limited, Hikaridai 3-4, Seika-cho, Kyoto 619-0237, Japan

shin1@kobe-kosen.ac.jp

Abstract. A monolayer of inorganic nanoparticles was fabricated on a silicon wafer using a cage-shaped protein, ferritin, which can sequester several types of inorganic nanoparticles in their cavities. Ferritins were bound electrostatically in an aqueous condition to the silicon wafer, which was modified with aminosilane molecules. We have used X-ray photoelectron spectroscopy (XPS) to study the effects of ion bombardment on a freshly cleaned ferritin surface. Compositional changes induced by 3.0 keV Ar⁺ sputtering in Fe₂O₃-ferritin nanoparticles have been quantitatively studied by XPS. All the Fe₂O₃-ferritin nanoparticles showed important changes to Fe nanoparticles in their stoichiometry for 60 sec with Ar⁺ sputtering. Furthermore, Kelvin force microscopy (KFM) has shown that there exists a very high surface potential, probably owing to the reduction of the surface to its element induced by Ar⁺ ion bombardment. With regard to the origin of the surface reduction activities, the induced surface potential is discussed.

1. Introduction

The cage-shaped protein, ferritin, is well known to uptake iron ions and forms a nanomeric uniform ferrihydrite (5Fe₂O₇.9H₂O) nanoparticle core in its cavity in vivo. Efforts to synthesize the nanoparticle of various materials in a hollow cavity in vitro have made it possible for ferritin to accommodate a variety of transition metal oxide and semiconductor cores [1,2]. Since the inner cavity size is restricted by the protein shell, the artificially biomineralized cores have uniformity in size and
shape. Moreover, ferritin can be placed on the desired area of the surface, and the protein shell can be selectively eliminated by utilizing the excellent advantages of proteins, such as the chemical flexibility of the protein surface and the vulnerability of the protein structure against heat/chemical treatment: we can produce a selectively deposited two-dimensional (2D) array of biomineralized nanodots.

In this paper, we present a comparative study of the compositional changes induced by 3.0 keV Ar$^+$ ion in Fe$_2$O$_3$ with X-ray photoelectron spectroscopy (XPS) and Kelvin Force Microscopy (KFM). The results for Fe$_2$O$_3$ indicate perfectly the reduction of oxides using high temperature in agreement with previously reported results [3]. In addition to the XPS study, we performed surface measurements by a KFM to find the difference in work function between Fe$_2$O$_3$ and Fe, which might be correspond to the particles of metal oxidation and pure metal observed by KFM.

2. Experimental details

2.1. Ar$^+$ ion bombardment by XPS

Ferritin (Fe$_2$O$_3$) nanopowder polycrystalline samples were used in this work. The adsorption of oxygen on clean metal surfaces has been the subject of many investigations in surface science (for a review, see refs. [4, 5]). Most of the work was dedicated to initially clean and highly defined single-crystal surfaces. In most industrial applications, however, the important processes occur under atmospheric conditions on polycrystalline surfaces exposed to air. In a previous work, we investigated the contact charging behavior of oxidized metal powders and pointed out the importance of the oxide layer on the electronic properties [6]. This was the motivation for an extended study of oxidized metal powders by means of different experimental techniques (XPS ULVAC-PHI 5500MT). Ferritin nanopowder polycrystalline samples were used in this work. Average nanoparticle sizes in the range of 7 nm for Fe$_2$O$_3$ were estimated by SEM in Fig. 1. Before Ar$^+$ etching, the samples, in the form of nanoparticles on the Si substrate, were cleaned in UV/O$_3$ treatment at 115 °C for 20 min to remove the absorbed water and other contaminants from their surfaces.

Fig. 1 (a) SEM image of deposited Fe$_2$O$_3$ core after protein elimination. Fe$_2$O$_3$ cores appear as white nanodots in the image. The inset depicts a schematic representation of the ferritin protein structure.
Sputtering was carried out in the preparation chamber of the spectrometer until a stationary state was reached for the shape of the XPS lines. A Penning Ar ion source working at 3.0 keV was used for this purpose. At regular intervals of ion bombardment XPS, spectra were recorded in a personal computer using MgKα (Fe and Fe₂O₃) as a X-ray sources. The analyzer grids were driven in the constant pass energy mode at 50 eV. For the Fe-containing samples, the reference of the binding energies (BE) was taken at Eb (Fe 2p₃/₂) = 706.75 eV, while for the Fe₂O₃ (2p₃/₂) 710.7 eV was used. The spectra were stored and processed in a computer in line with the spectrometer.

2.2. Samples preparation and KFM method

The Fe oxide (Fe₂O₃) core was synthesized biochemically in the genetically modified L-chain apoferritin hollow cavities with one-pot synthesis [1]. Following the deposition, the outer protein shell were removed by UV/O₃ treatment at 115 °C for 60 min. The mean core diameter (7 nm) is consistent with the ferritin cavity size and adsorption density of Fe cores is more than $5 \times 10^{11} \text{ /cm}^2$, which is as high as 80 % of the theoretical adsorption maximum. A schematic diagram of the experimental setup is shown in Fig. 2. KFM measurements were conducted in air using a SEIKO SPA 3800. The conditions used in this study were as follows: the resonance frequency was 23 kHz, and the spring constant was 1.6 N/m for the Au coated cantilever. In surface potential imaging, a modulation voltage with a frequency of 3 kHz and an amplitude of 0.8 Vrms was applied between the tip and the sample. The acquisition time for obtaining one image was about 20 min. All the images were taken in dark environment in order to avoid the photovoltaic effect.

Fig. 2 Schematic illustration of KFM setup for ferritin in air.
3. Results and Discussion

3.1 XPS measurement of Fe₂O₃ and Fe

Figure 3 shows the fitted XPS spectra of the Fe (2p_{1/2,3/2}) doublet from the original ferritin sample and after 60 sec of 3.0 keV Ar⁺ bombardment (i.e., stationary state). According to their binding energies, which agree with those in literature [7-10], Fig. 3 clearly shows the stepwise decomposition induced by the Ar⁺ bombardment. It is interesting to note that because of the presence of extra oxygen as contamination on Fe₂O₃ the intensity of the O (1s) signal shows a decrease larger than 90 % as sputtering proceeds. Fig. 3 shows the Fe (2p_{1/2}) XPS lines for the original surface and the stationary state (tₛ = 60 sec). From this figure it is clear that Ar⁺ bombardment induces the formation of some Fe⁰ (i.e., metallic phase) besides the original Fe²⁺ (i.e., Fe₂O₃). The relative concentrations of the two oxidation states of iron (marked A and B in Fig. 3(a)), as well as the peak area of the O(1s) level normalized to that in the original sample, are shown in fig. 3. In particular, the compositional change of embedded Fe cores was detected by X-ray photoelectron spectroscopy (XPS) measurement. The XPS spectrum from the embedded cores had two metal iron peak of A* and B*. Therefore, it is strongly suggested that the peaks of the Fe₂O₃ reduced the embedded cores to a metal state.

![Fe(2p) XPS spectra](image)

Fig. 3. XPS Fe₂O₃ (2p_{1/2,3/2}) spectra of original (a), and sputtered steady state of Fe (b), Peaks for the various states of chemical elements are indicated. Transition of peaks \( A \rightarrow A^* \), \( B \rightarrow B^* \).
3.2 KFM measurement of Fe₂O₃ and Fe

Figure 4 shows the topographic (a) and surface potential image (b) induced on the Fe₂O₃ nanoparticle on SiO₂/Si substrate before Ar⁺ ion bombardment, and surface potential image (c) induced on the Fe nanoparticle before Ar⁺ ion bombardment. We have no contrast in an image (b) of surface potential before Ar⁺ ion bombardment because work function between Fe₂O₃ and SiO₂ are very similar. The Fe and the silicon oxide surface was attenuate or cancel such potential difference. Figure 4 (d) shows the potential profile between the ferritin (Fe) and SiO₂ after Ar⁺ ion bombardmen. The surface potential profile (d) along the X axis was obtained from the surface potential image of (c).

Fig. 4 (a) topography, (b) surface potential induced on Fe₂O₃ polycrystal before Ar⁺ ion bombardment, (c) surface potential induced on Fe polycrystal by Ar⁺ ion bombardment, (d) The profile of the surface potential of (c) measured by KFM initially shows an abrupt increase at the start of bombardment.

The bottom region indicates the SiO₂ surface, in contrast, top region indicates the Fe surface. We paid attention to the potential drops between Fe and SiO₂. 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 20 mV. This change is probably caused by the bombardment of Ar⁺ ions. The KFM signal depends strongly on the work function of the material’s surfaces. The bombardment of Ar⁺ ions has effect of cleaning on the surface of the sample. But before taking the AFM images, the sample of nanoparticles on the Si substrate has already been cleaned in UV/O₃
treatment at 115 °C to remove the absorbed water and other contaminants from their surfaces. Therefore we think that the difference between work functions was visible. Stable KFM image have been obtained at high contrast and potential between Fe and SiO₂. It is suggested that surface Fe₂O₃ is located in a geometrically equilibrated position with the SiO₂ in an analogous to the behaviors of Fe oxidation, but moves to the non-equilibrated position under Ar⁺ ion bombardment. This results in the generation of the difference in work function and induced the surface charges. If this phenomenon causes the charge 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.

4. Conclusions

Compositional changes induced by 3.0 keV Ar⁺ bombardment of Fe₂O₃, have been quantitatively characterized by XPS. Fe₂O₃ resolves into two elements, which are Fe and oxide. From the present studies of the ion bombardment reaction of Fe₂O₃ to the type of Fe pure metals, we found new information about its mechanisms:

1) The XPS technique used in this study became a powerful tool for evaluating ion bombardment activities replacing chemical methods for ferritin during a very short time.

2) It has been suggested that the surface potentials measured using KFM may be induced by the metal oxide and metal surfaces appearing with increasing ion bombardment activity. Also, the work function induced by atomic displacements due to Ar⁺ creates the surface charges. It is suggested that this phenomenon causes a change in the surface potential of Fe; likewise, it may be a fundamental process responsible for the ion bombardment activity in other materials such as metal crystals.

We hope that this work not only demonstrates the experimental success of the fusion of biology and Si device processing but also opens the door to the biological path to the nanoelectronic devices.

References
[1] R. Tsukamoto, K. Iwahori, M. Muraoka and I. Yamashita: Bull. Chem. Soc. Jpn. 78 (2005) 2075.
[2] I. Yamashita, J. Hayashi and M. Hara: Chem. Lett. 33 (2004) 1158.
[3] T. Hikono, T. Matsumura, A. miura, Y. Uraoka, T. Fuyuki, M. Takeguchi, S. Yoshii, and I. Yamashita, Appl. Phys. Lett. 88 (2006) 023108.
[4] H. Kirimura, Y. Uraoka, T. Fuyuki, M. Okuda, I. Yamashita, Appl. Phys. Lett. 86 (2005) 262106.
[5] S. Yoshii, K. Yamada, N. Matsukawa, and I. Yamashita, Jpn. J. Appl. Phys. 44. No. 3(2005) 1518.
[6] A. Miura, T. Hikono, Takashi Matsumura, H. Yano, T. Hatayama, Y. Uraoka, T. Fuyuki, S. Yoshino, and I. Yamashita, Jpn. J. Appl. Phys. Lett. 45. (2006) L1-L3(2005) 262106.
[7] S. Hofmann and J. M. Sanz, J. Trace Microprobe Techn. 1 (1982-83) 213.
[8] N. Beathan, A. F. Orchard and G. Thornton, J. Phys. Chem. Solids 42186 (1981) 1051.
[9] H. F. Franzen, M. X. Umana, J. R. McCready and R. J. Thorn, J. Solid State Chem. 18 (1976) 363.
[10] N. Wagner, O. Brummer and N. Sauer, Cryst. Res. Technol. 17 (1982) 1151.