Morphological Change in FePt Nanogranular Thin Films Induced by Irradiation with 2.4 MeV Cu$^{2+}$ Ions: Electron Tomography Observation

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Electron tomography is a quite useful technique for characterization of shape and dispersion of metallic nanoparticles embedded in an amorphous oxide film.

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1. Introduction

Recently the areal density of magnetic recording media is rapidly increasing with reduction of size of magnetic grains, and it is expected to achieve 1Tbit/in$^2$ in the near future. However, the magnetic recording becomes unstable by thermal fluctuation if the size of magnetic grains gets smaller than a critical value. The critical size to superparamagnetism is generally reduced with enhancement of magnetic anisotropy. It is required to develop materials with high magnetic anisotropy to overcome the problem. It is well known that FePt alloys with the L1$_0$ ordered structure have such a high magnetic anisotropy as $K_{u} = 7 \times 10^6 \text{J/m}^3$, and the magnetization would be still stable even when the grain size is reduced into nanometer scale. Thin films with nanoparticles of FePt alloys are expected to be one of the promising candidates for the future ultrahigh density magnetic recording media. FePt nanogranular thin films are easily produced by the ion-beam sputtering technique. Since as-deposited FePt particles are usually of disordered facentered cubic (fcc) phase, the ordering of atomic arrangement into L1$_0$ should take place for magnetic recording applications. The ordered structure can be achieved by annealing at temperature higher than 870 K. However, such a high temperature annealing results in coarsening of particles at the same time. For the magnetic applications, thus we should control not only the ordering process but also other aspects such as size, shape and dispersion of nano-particles. In a previous study, we have examined the effects of 100 keV He-ion irradiation on structural changes in FePt nanogranular films with amorphous Al$_2$O$_3$ matrix. It has been revealed that He-ion irradiation significantly suppresses the growth of FePt nano-particles at an elevated temperature. Various phenomena of structural changes have been reported to be taken place by ion irradiation, depending on their mass and energy. For example, fragmentation of Au grains in a SiO$_2$ matrix is induced by irradiation with 4.5 MeV Au ions, resulting in inverse Ostwald ripening of the grains. On the other hand, swift heavy ions with such higher energy as a few hundred MeV are known to deform metallic particles embedded in an oxide amorphous layer. Thus ion-irradiation is expected as a tool for nano-structure modification of thin films.

The present study was conducted to examine the effect of irradiation with MeV-class ions on morphology of FePt granular films. To this end, we have employed electron tomography technique in transmission electron microscopy (TEM) to characterize their three dimensional structures in nanometer scale. The feasibility of electron tomography is also discussed in the present paper.

2. Experimental Procedure

FePt granular films were produced by ion beam sputtering of FePt and Al target under oxygen blow on Si(100) substrates. Nano-particles of FePt were dispersed in the matrix of amorphous Al$_2$O$_3$ of 20 nm thickness in the films. The composition of the films is (Fe$_{55}$Pt$_{45}$)$_{34}$(Al$_2$O$_3$)$_{59}$. Disks of 3.0 mm in diameter were cut out from the deposited films by an ultrasonic machine, and then the Si substrates were grounded to be about 100 µm thick. The disk specimens were once annealed at 923 K for 20 min (1.2 ks) in vacuum, and then irradiated with 2.4 MeV Cu$^{2+}$ ions up to $5 \times 10^{19}$ ions/m$^2$ at room temperature in a tandem accelerator at the Research Institute for Applied Mechanics, Kyushu University. The penetration range of 2.4 MeV Cu$^{2+}$ ions attains about 400 nm in an FePt alloy. It should be noted that most of irradiated Cu ions passed through the thin films. Some of the irradiated specimens were again annealed at 923 K for 1 h (3.6 ks) in vacuum to promote the L1$_0$ ordering in FePt particles. In addition, a reference specimen with coarsened FePt particles was prepared by annealing at 1023 K for 1 h (3.6 ks) in vacuum without ion-irradiation. The last speci-
men was utilized to confirm the feasibility of TEM tomography. To prepare thin films for TEM observation, the center portions of the Si substrate side were dimpled to 20 μm thick, and were then polished with Ar ions accelerated at 5 kV. A specimen for cross-sectional observation was also prepared by the mechanical grinding followed by the Ar ion milling. The microstructures of the films were examined by a JEM-2000EX TEM and a TECNAI-20 TEM, which were operated at 200 kV. The latter machine was mainly used for acquisition of images for electron tomography. A series of bright-field images were obtained at intervals of 2 degree from −60° to 60° of the tilt angle. Three-dimensional reconstruction of nanostructures was carried out, processing the tilt series of bright-field images by a standard software IMOD. The obtained results were displayed by a software AMIRA version 3.0.

3. Results and Discussion

3.1 Nanostructure in the as-deposited and annealed films

Figure 1 shows bright-field images of an as-deposited film viewed from two different directions. Here FePt particles are observed with dark contrast in the bright-field images, because the mass density is higher in the particles than in the matrix of amorphous Al₂O₃, and the mean scattering power for incident electrons of the former phase is much stronger than that of the latter. The averaged diameter of the particles is 2.3 nm for the as-deposited state. The diffraction pattern inserted in the upper right corner of (a) exhibits only Debye rings for fcc fundamental reflections, showing no incidence of ordering in the particles. In the cross-sectional view of (b), the deposited layer is confirmed to be 20 nm thick, coated with an epoxy layer for protection in the thinning process. Both sides of views in Fig. 1 clearly show that FePt nano-particles are uniformly dispersed within the deposited film.

Figure 2 demonstrates a result of 3-dimensional (3D) reconstruction of nanostructure in the as-deposited film. Here FePt particles appear with bright contrast, since the images are given in negative representation. In the original tilt series of 61 bright-field images, contrast change due to Bragg diffraction was recognized in particles at specific orientations. However, the diffraction effect on image contrast has not seriously disturbed the 3D reconstruction in the present processing. This is due to the fact that the image contrast arises significantly by difference in mass density between the particle and matrix phases, and the diffraction effect occurs for individual particles only in a limited number of 61 orientations. Thus the 3D reconstruction in Fig. 2 has successfully revealed the morphology within the film in nano-meter scale. Even so small particles as 1–2 nm in diameter are recognized in Fig. 2. One may again confirm the uniform dispersion of particles inside the as-deposited film.

Figure 3 shows 3D morphology in a film annealed at 923 K for 20 min (1.2 ks). One can recognize clearly coarsened FePt particles. The mean diameter of particles has increased to 6.4 nm by the annealing. Additional Debye rings were recognized in the corresponding diffraction pattern, indicating that the ordering to L₁₀ has taken place in the particles. Figure 4 gives cross-sectional representations of a part of the 3D reconstructed image in Fig. 3. FePt particles are clearly seen in the lateral cross-section on an x–y plane, while the contrast becomes blurring in the vertical cross-sections including z-direction of foil-thickness. The degrading of image contrast in the z direction should be ascribed to the missing wedge of information caused by the limited range of tilting in acquisition of original TEM images. The resolution along the vertical direction in a 3D reconstructed image is degraded by a factor in comparison with that in the x–y plane, when the tilting range is limited to ±α radian. The value of e is evaluated to be 1.55 for the present condition, being responsible for fuzzy
contrast of top and bottom parts of the particle interface perpendicular to the $z$-direction. The particles observed in Fig. 4 are regarded as almost isotropic and any distinct tendency of directional growth is not recognized. A 3D morphology after annealing at 1023 K for 1 h (3.6 ks) is demonstrated in Fig. 5. A longer annealing at a higher temperature naturally proceeds further growth of particles, and the averaged size of them has reached about 50 nm in diameter. The coarsened particles look weakly faceted in Fig. 5, in contrast to smaller ones observed in the preceding figures. The facet planes were revealed to be parallel to $\{011\}$ by high resolution TEM observation. The similar faceting
tendency has been recognized in octahedron shaped FePt particles epitaxially grown in an FePt/MgO multilayer. Thus electron tomography is quite useful to identify 3D shape and dispersion of FePt nano-particles.

### 3.2 Nanostructure change due to ion-irradiation

In Fig. 6 one may compare bright field images and selected area diffraction patterns of FePt granular films before and after irradiation with $5 \times 10^{19}$ ions/m$^2$ of 2.4 MeV Cu$^{2+}$ at room temperature. The bright field images show no remarkable change due to ion irradiation, except that the outlines of the particles get more defined and rounded, and the image contrast becomes pronounced. The mean diameter of particles is slightly reduced from 6.4 to 5.6 nm by irradiation. The Debye rings of superlattice reflections are missing in the diffraction pattern after irradiation. It simply indicates that the ion irradiation results in disordering in FePt nanoparticles.
as many as 0.4 dpa in the FePt alloy phase. However, this value of dpa seems too small to bring about the striking shape change of particles. It is not reasonable to ascribe only the knocked-on displacements to the elongation of FePt particles.

D’Orellán et al.\textsuperscript{11–13} recently reported that irradiation with 200 MeV \textsuperscript{27}Al ions up to $1 \times 10^{18}$ ions/m\textsuperscript{2} causes elongation of implanted Co nanoparticles in a SiO\textsubscript{2} layer along the beam direction. They have attributed the particle deformation to the thermal spike effects characteristic to the swift heavy ion irradiation. Heavy ions accelerated to an energy in the range of a few hundreds MeV causes strong electronic excitation locally along their trajectories, resulting in extreme rise in temperature and in pressure within cylindrically shaped regions around the ion tracks. The particles are therefore instantly melt and pressurized when swift heavy ions pass through, and are then deformed along the ion tracks. However this scenario is not simply applied to the present case, since the energy of irradiated ions is not so high as local melting occurs significantly. On the other hand, ion irradiation with a lower energy of MeV-order is known to deform micrometer-sized spherical colloidal particles to be oblates with an anisotropic growth perpendicular to the beam direction.\textsuperscript{19} This deformation process is described by the so-called “ion-hammering” effect associated with local stress set up by flash-heating along the ion tracks.\textsuperscript{20,21} The ion-hammering effect due to irradiation with 2.4 MeV Cu\textsuperscript{2+} ions is likely to give rise to stress perpendicular to the beam direction in the amorphous Al\textsubscript{2}O\textsubscript{3} matrix, and to play a role in the anisotropic deformation of FePt particles. However, it should be noted that the averaged volume of particles has increased by a factor of about 1.3 by irradiation. The volume change of particles due to irradiation cannot be explained solely in terms of the ion-hammering effect. More detailed experiments and analyses are now under investigation to clarify the mechanism of deformation of nano-particles.

Figure 9 shows a bright field image and the corresponding electron diffraction pattern of a specimen subjected to post-irradiation annealing at 923 K for 1 h. The diffraction pattern weakly indicates that the re-ordering to $L1_0$-type order dispersing in a thin film by combination of ion-irradiation and heat-treatments. Magnetic properties of the films are now being measured as a function of 2.4 MeV Cu-ion irradiation and heat-treatments. The results will be reported elsewhere.

4. Conclusions

The present study was conducted to investigate the effects of irradiation with 2.4 MeV Cu\textsuperscript{2+} ions on nano-structure in FePt granular thin films with amorphous Al\textsubscript{2}O\textsubscript{3} matrix. To this end we made a trial to employ the electron tomography technique with a tilt series of TEM images to identify 3-dimensional nano-structure in the films. It has been demonstrated that electron tomography is quite useful to characterize shape and dispersion of metallic nanoparticles embedded in an amorphous oxide film with a high spatial resolution. Electron tomography images clearly revealed that the

Figure 6 Bright field images and selected area diffraction patterns of (FePt)$_{(30)}$(Al\textsubscript{2}O\textsubscript{3}) before (a) and after (b) irradiation with $5.0 \times 10^{19}$ ions/m\textsuperscript{2} 2.4 MeV Cu\textsuperscript{2+} ions.

Figure 7(a) shows 3D reconstructed tomography images of the irradiated film viewed in various orientations. It should be noted that the particles are significantly elongated along the direction of film thickness, which is parallel to trajectories of irradiated ions. Cross-sectional views of one FePt particle are illustrated in Fig. 7(b). This particle is in a rod-shape of 5 nm in diameter and 20 nm in length. As FePt particles were almost isotropic before irradiation as shown in Figs. 3 and 4, it is evident that the irradiation with 2.4 MeV Cu\textsuperscript{2+} ions causes the elongation of particles. The image contrast enhancement due to irradiation, which is seen in Fig. 6, is explained in terms of their elongation along the viewing direction. The distribution of particle lengths measured in tomography images is characterized by the averaged length of 11.2 nm and the standard deviation of 3.5 nm, as shown in Fig. 8. As the mean diameter is 5.6 nm, the aspect ratio of particles reaches 2.0 on average by the ion-irradiation. According to SRIM calculation,\textsuperscript{18} the present condition of ion-irradiation leads to knocked-on displacements of atoms...
irradiation with 2.4 MeV Cu\(^{2+}\) ions causes anisotropic deformation of FePt nanoparticles with elongation along the direction of ions trajectory and slight shrinkage in the perpendicular directions. Ion-irradiation results in disordering in FePt, but post-irradiation annealing at 923 K for 1 h (3.6 ks) leads to re-ordering without significant coarsening and shape change of FePt particles. Thus it has been suggested that one may control the state of order, shape and dispersion of FePt nanoparticle by combination of ion-irradiation and heat treatments.

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