**In-situ** Electron Holography Observation of FePt Nanoparticles at Elevated Temperatures

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We have developed a method to observe the magnetic field around L₁₀ FePt nanoparticles by **in-situ** electron holography at elevated temperatures. FePt Nanoparticles with sharp size distribution and chemical homogeneity were synthesized by the reverse micelle method. The as-prepared FePt nanoparticles, which had a disordered fcc structure (A₁) with the diameter centered at 6 nm, were coated with a surfactant, dispersed onto a glass plate, and heated in order to undergo a transformation from A₁ to an ordered fct structure (L₁₀). The particles were kept separated by the surfactant with their original diameter during annealing. A submicron-size island comprising isolated particles was removed and dispersed on an electron transparent carbon film and then magnetized along one direction. We observed a magnetic field distribution of the submicron-size island of nanoparticles by means of electron holography during heating. Although magnetization decreased between 212°C and 412°C to 25% of the initial strength at 25°C, the magnetization diminished and did not recover again during cooling. The Curie temperature (Tc) of the FePt nanoparticles was determined to be 350°C and was in good agreement with the Tc determined by bulk measurements using a VSM, which was approximately 100°C lower than the reported Tc for bulk Fe₅₆Pt₄₄. [doi:10.2320/matertrans.MD200703]

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1. Introduction

L₁₀ FePt alloy has attracted attention in recent years and it is expected to be an excellent magnetic material for high-density magnetic recording because of its high magnetocrystalline anisotropy.¹,²

Thus far, most L₁₀ FePt nanoparticles have been prepared by the annealing of films manufactured by sputtering or evaporation.³⁻⁸ Sun et al. prepared FePt nanoparticles by reducing Fe(CO)₅ and Pt(acac)₂ in an organic solution at high temperatures.⁹ The as-prepared nanoparticle had a paramagnetic A₁ structure, which was transformed to ferromagnetic L₁₀ during high temperature annealing.

It is important to determine the temperature dependence of the magnetism of nanoparticles in order to understand the manufacturing process and improve the stability of magnetization in nanoparticles.

Electron holography is a useful method for observing electromagnetic fields in microscopic areas because the fields are displayed as equal-phase lines of object waves in interference micrographs.¹⁰ It has been applied to visualize magnetic fields in thin films¹¹ and small particles.¹²

In order to observe a magnetic field distribution around small particles at a nanometer scale, Yamamoto et al.¹³ developed an improved phase-shifting electron holography technique and observed magnetic fields around the tip of fine iron particles with diameters of 30 nm. However, in this method, it is necessary to obtain many holograms and the analysis is fairly complicated. Thus far, it is difficult to observe magnetic fields around a particle with a diameter of several nanometers.

Many studies have been performed to evaluate the temperature dependence of magnetic thin films¹⁴,¹⁵ and particles¹⁶ during heating in a TEM near the Curie temperature. However, the temperature dependence of the magnetism of nanoparticles with diameters of several nanometers has not yet been reported.

The magnetic properties of nanoparticles evaluated by bulk measurements depend not only on their size and size distribution but also on their chemical composition.¹⁷,¹⁸ Unfortunately, in previous studies,³⁻⁹ neither the size distribution nor the chemical homogeneity of the particles was reported explicitly.

Therefore, it is not clear whether the magnetic properties of nanoparticles are governed by the differences in size distribution and/or chemical homogeneity.

Recently, some of the present authors succeeded in preparing FePt nanoparticles with chemical homogeneity and monodispersion by the reverse micelle method. These nanoparticles exhibited high coercivity after thermal annealing.¹⁹,²⁰

The objective of this study is to develop a method to evaluate the temperature dependence of the magnetic properties of FePt nanoparticles by electron holography. Although it is impossible to determine the magnetic properties of an individual particle, those of an island comprising few hundreds to few thousands of nanoparticles would be representative of an individual nanoparticle. We have performed an **in-situ** electron holography observation of an island of nanoparticles with monodispersion magnetized along a single direction.

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2. Methods

2.1 Preparation of FePt nanoparticles

FePt nanoparticles were synthesized by the reverse micelle method.\textsuperscript{19,20} The particle size was measured using a Hitachi HF-2200 field emission gun transmission electron microscope (FE-TEM) operated at an accelerating voltage of 200 kV. The chemical compositions of individual nanoparticles were analyzed using a NORAN VANTAGE energy dispersive X-ray spectrometer attached to the HF-2200. For the bulk chemical analysis, the FePt nanoparticles were dissolved in nitrohydrochloric acid and the contents of Fe and Pt were analyzed using a Shimadzu ICPS-1000IV inductively coupled plasma-optical emission spectrometer (ICP-OES).

Figure 1 shows the shapes and chemical compositions of the FePt nanoparticles. As indicated by the TEM micrograph (Fig. 1(a)), the average diameter of the particles was 6 nm with a very sharp size distribution. The contents of Fe and Pt as determined by FE-TEM/EDS were 46 ± 6 and 54 ± 6 at%, respectively, as shown in Fig. 1(b). The bulk contents of Fe and Pt as determined by ICP-OES were 47 and 53 at%, respectively. The Fe and Pt contents of the individual particles were in good agreement with the bulk contents within an experimental error.

2.2 Sample preparation

The FePt particles were mixed with a surfactant, which is an organic polymer containing Si and O, in order to inhibit aggregation during annealing and were dispersed onto a glass plate and dried. The sample was annealed at 525°C in an N\textsubscript{2} + 4%H\textsubscript{2} atmosphere for 30 min. This sample was used for bulk magnetization measurements by a vibration sample magnetometer (VSM).

The particles were removed from the plate and dispersed onto a carbon thin film covering a Cu grid. The specimen was magnetized at 5.6 MA-m\textsuperscript{-1} by an electromagnet that was parallel to the film surface and then used for electron holography. In order to avoid charging up, a carbon film with a thickness of a few nanometers was deposited on both sides of the specimen.

2.3 Bulk magnetization measurement

The bulk magnetization measurements were performed using a TOEI VSM-5 vibration sample magnetometer under a pressure of 10\textsuperscript{-5} Pa. Magnetic hysteresis loops were measured in a magnetic field range of ±1 MA-m\textsuperscript{-1} at a sweep rate of 200 kA-m\textsuperscript{-1}.min\textsuperscript{-1} with a time constant of 1 s. The specimen was heated in a quartz heating cell to 550°C. The relation between temperature and magnetization (M-T curve) was measured in a magnetic field of 800 kA-m\textsuperscript{-1}, where the magnetization saturates to a magnetization referred to as Ms, in a temperature range of 25–550°C at a sweep rate of 250°C.h\textsuperscript{-1}. In the analysis of the results obtained from these measurements, the magnetization of a quartz plate was subtracted from that of the sample as background.

2.4 In-situ electron holography experiment

Electron holography observation was performed using a HF-2000 TEM equipped with a low magnetic field pole piece, an electron bi-prism, and Gatan794 slow scan CCD, and operating at an accelerating voltage of 200 kV. The specimen was heated on a double tilting heating holder to 512°C. The relation between the current and the heating element temperature without a sample was obtained beforehand using an optical pyrometer outside a TEM and was further calibrated by measuring the melting points of Al, Sb, and Pb thin films using a TEM. The observations were performed at each 100°C rise between 212 and 512°C. At each temperature, the electric current of the heater was maintained constant for 1 h such that the specimen attained thermal stability and equilibrium. Electron holograms were analyzed using Avision software AV-FTPHA of Image Sense Co., Ltd.
3. Results

3.1 Shapes and crystal structures of FePt nanoparticles

Figures 2(a) and (b) are TEM micrographs of the particles before and after annealing, respectively. The size of the FePt particle was not changed during annealing. The surfactant inhibited the aggregation of particles as a barrier. The chemical homogeneity of the particles was also maintained during annealing (not shown here).

Figure 2(c) shows a typical electron diffraction pattern of the Fe-Pt nanoparticles before annealing. The diffraction rings were indexed as \{111\}, \{200\}, \{220\}, and \{311\} of A1. After annealing (Fig. 2(d)), the diffraction rings, which became spotty, were indexed as \{001\}, \{110\}, \{111\}, \{002\}, \{201\}, \{112\}, \{202\}, \{113\}, and \{222\}. Among them, \{001\}, \{110\}, \{201\}, and \{112\} are uniquely attributed to the ordered L10 structure. Therefore, the phase transformation from A1 to L10 occurred during annealing.

3.2 Bulk magnetization measurement

The VSM measurement of FePt nanoparticles coated on a quartz plate before annealing had a small value of Ms and did not exhibit hysteresis (not shown here). The size of the FePt particle was not changed during annealing. The surfactant inhibited the aggregation of particles as a barrier. The chemical homogeneity of the particles was also maintained during annealing (not shown here).

Figure 3(b) shows the temperature dependence of Ms, which was measured from the FePt nanoparticles coated on a quartz plate after annealing at 800 kA•m\(^{-1}\) by a VSM in vacuum. The magnetization was constant at low temperature range and decreased along a sigmoidal curve while the temperatures were elevated higher than \(\approx 200^\circ\)C. Tc was determined as the temperature where the second derivative of the M-T curve was zero and was found to be \(330^\circ\)C.

3.3 Electron holography of islands of FePt nanoparticles

Figures 4(a) and (b) show an electron hologram of an island of FePt particles with sizes of \(\approx 1\) \(\mu\)m and a phase image reproduced from the electron hologram, respectively. Figure 4(c) is an enlarged phase image around the island. Figures 4(d) and (e) show an electron hologram of an island of FePt particles with sizes of \(\approx 500\) nm and a phase image reproduced from the electron holograms, respectively. Figure 4(f) is an enlarged image of a phase image around the island. In Figs. 4(b), (c), (e), and (f), the contour fringes in the phase images began and ended at points on both sides of the island. The contour fringes can be interpreted as the magnetic lines of force.\(^{21}\) The dotted arrow indicates the line that passes through these two points. An open bold arrow indicates the magnetization direction of the external magnetic field before TEM observation. The directions of these two arrows were in good agreement with each other. From these results, it is apparent that the magnetic field around an island was detectable. The smallest size of the islands around
which the magnetic field can be detected was 200 nm; these islands are believed to contain ca. 2000 particles. This detection limit corresponds to a magnetic flux of $9 \times 10^{-15}$ Wb. The fields of closely spaced particles that were magnetized along a single direction were summed and then a detectable field was formed.

### 3.4 In-situ electron holography of FePt nanoparticles

Figure 5(a) shows an electron hologram of an island of FePt particles with diameters of $\sim 1 \, \mu m$. Figures 5(b), (c), (d), and (e) show phase images at 25°C before heating and those at 312°C, 412°C, and 25°C after heating, respectively. The decrease in the number of contour fringes indicates the reduction in the magnetization of the particles during heating.

Figure 6 shows the temperature dependence of the maximum phase shifts across the centre of the island of FePt particles. The magnetization decreased at temperatures higher than 200°C and the strength was reduced to 25% of the
initial strength at 412°C; however, it increased during cooling and recovered 67% of its initial strength at 25°C.

Figure 7(a) shows an electron hologram of an island of FePt particles with sizes of ~500 nm. Figures 7(b), (c), (d), (e), and (f) show phase images at 25°C before heating and those at 312°C, 412°C, 512°C, and 25°C after heating, respectively. The decrease in the number of contour fringes indicates the reduction in the magnetization of the particles during heating.

Figure 8 shows the temperature dependence of the maximum phase shifts across the center of the island of FePt particles. When an island was heated to 512°C, the magnetization did not recover during cooling. The M-T curve was fitted with a spline function. The Curie temperature (Tc) was determined as the temperature where the second derivative of the fitted curve was zero and was found to be 350°C. It was approximately 100°C lower than the reported Tc of bulk Fe_{55}Pt_{45}. It was in good agreement with the Tc determined by VSM.

4. Discussion

Figure 9 shows the proposed scheme for the explanation of the magnetic states of an island comprising FePt nanoparticles. The truncated circles indicate the particles. A pair of short lines, which truncates the circle, indicates {001} planes (in the inset a blank arrow indicates the c-axis). The arrow in the truncated circle indicates the magnetic moment.
Fig. 8 Temperature dependence of the maximum phase shift across the center of the particle island with sizes of ~500 nm.

Fig. 9 Schematic diagram of the magnetization orientation in individual nanoparticles at (a) 25°C before heating, (b) 412°C and (c) 25°C after heating to 412°C, and (d) 512°C and (e) 25°C after heating to 512°C.

included in the particle. While the particles are magnetized by applying an external magnetic field, the direction of the magnetic moment included in each particle is along the direction of the external magnetic field. (a) shows a magnetic state of an island after the removal of the external magnetic field. Because the direction of the easy magnetization of L1₀ FePt crystalline is c-axis, the residual magnetic moment included in each particle after the removal of the external magnetic field is oriented along the c-axis. Because the external magnetic field once applied was strong enough to attain a magnetic saturation, the strength of the magnetic moments are almost identical between the particles. The bold arrow on the left side of the island indicates the sum of the magnetic moments included in each particle, which is along the direction of the once applied external magnetic field.

At 412°C ((b)), the magnetic moments of each particle are weakened and a part of the magnetic moments is inversed (as the dotted arrow in a particle indicates) by thermal fluctuation. As a result, the sum of the magnetic moments along the direction of the once applied external magnetic field is (as the bold arrow on the left side of the island indicates) also weakened. During cooling from (b) to (c), the strength of the magnetic moment included in each particle is recovered. However, because a part of the direction of the magnetic moments has been inversed, the sum of magnetic moment along the direction of the once applied external magnetic field was recovered to 67% of the initial strength. Because the inverted magnetic moments are a small part of the particles, the direction is probably unchanged from the initial direction.

At 512°C ((d)), all magnetic moments are weakened to zero by thermal fluctuation. During cooling from (d) to (e), the intensities of magnetic moments of particles are recovered. However, because the directions of magnetic moments are random, they are summed up to zero along the initial direction.

The reported Tc of bulk Fe₅₅Pt₄₅ is 497°C. The Fe and Pt contents of the FePt nanoparticle were similar to that of this bulk sample. The Tc of FePt nanoparticles was probably lower than that of the bulk sample due to the large surface ratio of nanoparticles. An increase in the fraction of atoms on the surface leads to a decrease in the correlation distance. As a result, particles are transformed to the superparamagnetic state at a lower temperature.

The magnetization of nanoparticles exhibited a gradual decrease across a wide temperature range. This decrease cannot be explained by the sharp size distribution and chemical homogeneity since these are retained during annealing. With regard to the grain structure of individual particles, two apparent types were evident (Fig. 2(b)): one is single crystalline and the other is twinned. The above-mentioned grain structure could be responsible for this gradual decrease.

The final objective of the development of electromagnetic devices of FePt is to realize the construction of devices with a single nanoparticle; devices containing between few hundred and few thousand particles will be developed and commercialized in the near future.

In order to analyze the magnetic structure in magnetic devices, several methods are used. VSM and SQUID are widely used for bulk measurements. However, it is not possible to evaluate microstructures. Magnetic force microscopy is one of the methods, which are used to observe microscopic magnetic structures. However, because the measured magnetic properties depend on temperatures and probes are instable at high temperatures, it is not easy to evaluate a distribution of magnetic fields at high temperatures.

The method we have developed will be applicable not only for evaluating the magnetic properties of nanoparticles and nanostructures quantitatively but also for characterizing the properties of microelectromagnetic devices especially at high temperatures.

5. Concluding remarks

We have developed a method to observe the magnetic field around L1₀ FePt nanoparticles by in-situ electron holography at an elevated temperature. The temperature dependence of the magnetic field around a submicron-size island comprising isolated FePt nanoparticles with a sharp size distribution and
chemical homogeneity was evaluated by means of electron holography observations during heating. The magnetization decreased at temperatures higher than 200°C. When heated to 512°C, the magnetization reached zero and did not recover during cooling. The Curie temperature of the FePt nanoparticles was determined to be 350°C, which was in good agreement with the Tc determined by VSM measurements. It was approximately 100°C lower than the reported Tc for bulk measurements. The lower temperature is probably due to the surface effect that enhances the transformation from the ferromagnetic state to the superparamagnetic state.

By using this method, it is possible to evaluate the temperature dependence of the magnetic properties of an assembly of individual L1₀ FePt nanoparticles at a micrometer scale with considerable stability.

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REFERENCES