Effect of structural transition on the temperature-dependent magnetic properties of epitaxial FePd alloy nanoparticles

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Abstract. We have studied atomic ordering and magnetic properties of epitaxial FePd nanoparticles 3-14 nm in diameter. Thermal fluctuation of magnetic moment of $L_1^0$-FePd nanoparticles becomes prominent when particle size is smaller than about 8 nm. Atomic images of high-resolution transmission electron microscopy revealed the formation of the ordered phase in FePd nanoparticles as small as 4 nm in diameter, while the superlattice reflections were quite weak compared to those of the larger sized particles (>8nm). The experimental results indicate that the degradation of magnetic anisotropy is induced by the size-dependent decay of long-range atomic order.

1. Introduction

The demand for higher density magnetic recording media is one of the fundamental motivations for the recent attentions to hard magnetic nanoparticles that are characterized by high magnetocrystalline anisotropy energy (MAE) [1]. One of the candidates for ultrahigh density magnetic storage media is FePd alloy nanoparticles with the $L_1^0$-type ordered structure. The hard magnetic properties of the $L_1^0$-FePd alloy nanoparticles originate from the tetragonal ordered structure with a high MAE [2], and thus the atomic ordering and the stability of the ordered phase are key issues. According to our previous work [3], the degree of order depends on particle size and the decrease of the long-range order (LRO) parameter was found for FePd nanoparticles below 8 nm in diameter. The latest atomic resolution imaging based on the aberration-corrected high-resolution transmission electron microscopy (HRTEM) also revealed a loss of clear-cut LRO for particles 2-5 nm in size [4]. Such a depression of LRO, namely, structural transition towards disordered phase, is a size-dependent event frequently observed in nanoparticles, and will lead to a rapid decrease in MAE. The effect of particle size including such a size-dependent structural transition on magnetic properties can be detected by measuring temperature dependence of magnetization. Understanding of the aforementioned size-dependent phenomenon may also contribute to the recent high-density magnetoresistive random access memory (MRAM) using a thin $L_1^0$-ordered layer as well as a magnetic storage media.

This study aims at clarifying particle size dependence of magnetic properties of epitaxial FePd nanoparticles at the onset of the structural transition. We show that superparamagnetic behavior becomes prominent when a clear-cut LRO is lost. Thermal relaxation of remanent magnetization is discussed based on the particle size distribution.
2. Experimental Procedure

FePd nanoparticles were fabricated by sequential electron-beam deposition of Pd and Fe onto NaCl (001) single crystal substrates at substrate temperature $T_s$ of 476-673 K (base pressure of $1 \times 10^{-6}$ Pa) [5]. After the deposition of Fe, a 10-nm-thick amorphous film of Al$_2$O$_3$ was deposited at a substrate temperature of 523 K to protect the particles. Postdeposition annealing was performed in a high vacuum quartz-tube furnace ($2 \times 10^{-5}$ Pa) for 3.6ks at 873 K. Particle morphology and atomic structures were observed by using 200 kV (JEOL JEM-2010) and 300 kV (JEM-3000F) electron microscopes. Compositional analysis was carried out by using an energy dispersive x-ray spectrometer (EDS) attached to the 300 kV-TEM. Magnetic properties, including hysteresis loops, temperature dependence of magnetization, and remanent magnetization decay, were measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL) in the temperature range between 10 and 300 K with a magnetic field up to 50 kOe. The magnetic field was applied perpendicular to the film plane. The measuring time was set to be 10 sec in this study.

3. Results and discussion

3.1 Particle morphology and atomic structure

Figure 1 shows the bright-field (BF) TEM images and the corresponding selected area electron diffraction (SAED) patterns of FePd nanoparticles after annealing for 3.6 ks at 873 K. Substrate temperature ($T_s$) and the average particle size ($d$) are as follows: (a) $T_s = 573$ K, $d = 8.2$ nm, (b) $T_s = 473$ K, $d = 4.3$ nm, respectively. Histograms of particle size distribution of the FePd nanoparticles followed a log-normal-type distribution function. Note that size distribution becomes narrower as the average size reduces. In fact, as can be seen in the histogram of Fig. 1(b), a quite sharp distribution has been realized for nanoparticles 4.3 nm in average size. In the [001] incidence of the L1$_0$ structure, four-fold 110 superlattice reflections can be seen on an SAED pattern. In fact, the SAED pattern in Fig.1(a) clearly indicates a formation of the L1$_0$ structure with preferential c-axis orientation normal to the film plane. Noticeable feature here is the intensity of the superlattice reflections: the intensity is

Figure 1 TEM images and the corresponding SAED patterns for (a) 8-nm-sized and (b) 4-nm-sized FePd nanoparticles after annealing. Histograms of particle size distribution are also shown in the inset. In Fig.1(b), an example of the HRTEM image of a locally ordered particle is also shown.
quite weak for nanoparticles shown in Fig.1(b). This result clearly indicates the size-dependent degradation of the LRO in FePd nanoparticles as confirmed by our previous work using nanobeam electron diffraction [3]. We confirmed atomic structures of these 3-4-nm-sized nanoparticles by HRTEM observation. As a result, faint {110} lattice fringes, due to alternate stacking of Fe and Pd in the [001] direction, were still observed, in accordance with the latest HRTEM study using an aberration corrector [4]. An example of HRTEM image of a 4-nm-sized particle is shown in the inset of Fig.1(b).

3.2 Size and temperature-dependent magnetic properties

Figure 2(a) shows the average particle size dependence of the coercivity measured at 300 and 10 K with the external magnetic field perpendicular to the film plane. Coercivity as high as 3.5 kOe was obtained for larger sized particles (>11nm), while the coercivity abruptly dropped in the particle size range between 8 and 10 nm. The coercivity reached quite low values (<200 Oe) for particles smaller than 6 nm. Such an apparent decay of coercivity with size reduction below 10 nm can be attributed to superparamagnetic behaviour, namely appearance of thermal fluctuation of magnetization. Noticeable feature here is the size dependence of coercivity at 10 K. As shown in Fig.2(a), the coercivity at 10 K also drastically decreased similar to those at 300 K, indicating the degradation of MAE with size reduction. Note that there are two kind of characteristic particle size regions: one is the region between 6 and 8 nm that is characterized by the decrease in LRO [3]. The other is the region between 2 and 5 nm, where local ordering, indicated by faint superlattice reflections and loss of clear {110} fringes, appeared as shown in Fig.1(b). The rapid decrease in coercivity was observed at the former size region, indicating the loss of magnetocrystalline anisotropy triggered by the decay of LRO. Figure 2(b) shows average particle size dependence of the coercivity ratio, $H_c(10K)/H_c(300K)$. There observed a jump in the region at around 8 nm in diameter, clearly indicating the fact that the effect of thermal fluctuation on coercivity becomes prominent below 8 nm.

![Figure 2](image.png)

Figure 2 (a) Average particle size dependence of coercivity for FePd nanoparticles after annealing at 3.6ks for 873K. Coercivity abruptly dropped in the particle size range between 8 and 10 nm. (b) Size dependence of the coercivity ratio, $H_c(10K)/H_c(300K)$.

To further confirm the effect of thermal fluctuation, we measured field-cooling (FC) and zero-field-cooling (ZFC) magnetization curves in the temperature range between 10 and 400 K. Figures 3(a) and 3(b) show the FC and the ZFC curves for FePd nanoparticles with average sizes of 8.2 nm and 4.3 nm, respectively. The magnetic field of 100 Oe was applied perpendicular to the film
plane. In Fig. 3(a), the ZFC curve increases monotonously as the temperature increases, and showed a very broad, faint peak approximately at 350 K. Relatively high blocking temperature observed for the 8-nm-sized particles can be attributed to the coexistence of superparamagnetic and ferromagnetic components, depending on the particle size. By decreasing the average particle size to 4.3 nm, blocking temperature shifts towards the lower temperature and a clear peak appeared at 100 K in the ZFC curve as shown in Fig. 3(b). The observed sharp peak can be attributed to the narrower particle size distribution (Fig. 1(b)). The FC curve almost overlapped with the ZFC curve for nanoparticles 14 nm in average size in the whole temperature range between 10 K and 400 K. Thus it has been revealed that the thermal fluctuation of magnetic moment becomes prominent when the particle size is smaller than about 8 nm in diameter, as confirmed by the abrupt reduction of coercivity, jump in coercivity ratio, and the appearance of blocking temperature.

3.3 Size-dependent thermoremanent magnetization decay

Figure 4(a) shows remanent magnetization decay measured at 300 K for FePd nanoparticles with different average sizes. Magnetic field of 50 kOe was first applied perpendicular to the film plane, and then, immediately removed the field, followed by the measurement of the thermoremanent magnetization (TRM) decay. All the TRM curves decrease logarithmically irrespective of the average particle size, but with different slopes, due to thermal fluctuation of magnetic moment. The gradient of the decay curves increase as the average particle size becomes smaller, which can be attributed to the enhancement of thermal fluctuation in smaller sized particles due to the degradation of MAE triggered by the size-dependent reduction of LRO. It should be noted that particle areal density also plays a crucial role on the relaxation behaviour of nanoparticles, since the relaxation time can be affected by interparticle magnetostatic interaction, which is determined by geometrical arrangement of magnetic

![Figure 3](image1.png)

**Figure 3** ZFC and FC curves for (a) 8-nm-sized and (b) 4-nm-sized FePd nanoparticles after annealing at 3.6ks for 873 K. The applied field was 100 Oe in the film normal direction.

![Figure 4](image2.png)

**Figure 4** (a) Remanent magnetization decay curves for different sized FePd nanoparticles measured at 300K. All the specimens were annealed for 3.6ks at 873K. (b) Temperature dependence of the viscosity parameter (S) for different sized FePd nanoparticles. A peak position shifts towards lower temperatures as the particle size reduces.
particles and distribution of easy axis orientation. In the present experiment, the particle density decreased from $3.2 \times 10^{11} \text{ cm}^{-2}$ to $1.9 \times 10^{11} \text{ cm}^{-2}$ as the average particle size reduced from 8.2 nm to 4.3 nm in diameter. Such a reduction of the particle density will lead to weaken the magnetostatic interaction among the nanoparticles, while the details still remain open question.

To examine the temperature dependence of the decay of TRM, we measured the decay curves at different temperatures between 10 and 350 K. The gradient of the decay curve, so called the magnetic viscosity parameter ($S$) [6], is expressed by the following logarithmic form [6,7],

$$M_r(t) = M_0 - S \ln t$$

where $M_r(t)$, $M_0$, and $t$ denote the time-dependent remanent magnetization, the initial remanent magnetization, and the time, respectively. Figure 4(b) summarizes the parameter $S$ for two kinds of specimens, 8.2 nm and 4.3 nm in average sizes. For the larger particles, the viscosity parameter shows the maximum at 250 K, while that of the smaller one at 50 K. The origin of such maximum peaks can be attributed to the distribution of relaxation time due to particle size distribution. Note that the amount of relaxation is small at very low temperatures, and small as well at higher temperatures, since most of the small particles with short relaxation times will reach thermal equilibrium within the experimental measurement time at higher temperatures. Thus, a peak appears in the temperature dependence of the viscosity parameter. The smaller particles have shorter relaxation times; hence, the peak temperature shifts towards lower temperatures as the average size reduces. The present study hence demonstrates the degradation of MAE triggered by the size-dependent reduction of LRO (<8nm), and it is further enhanced by the decay of clear-cut LRO (<5nm). To overcome the effect of thermal fluctuation, proper heat treatment for realizing sufficiently high degree of order will be effective, as indicated by recent literatures [8-10].

4. Conclusion

In conclusion, we demonstrated that the hard magnetic properties of epitaxial L1$_0$-FePd nanoparticles are largely affected by the particle size and temperature. Thermal fluctuation of magnetic moment of L1$_0$-FePd nanoparticles becomes prominent when particle size is smaller than about 8 nm, due to the size-dependent reduction of the LRO parameter. The coercivity reached quite low values (<200 Oe) for particles smaller than 6 nm, in accordance with the loss of clear-cut LRO as observed by HRTEM (<5nm). The present study clearly showed the degradation of MAE triggered by the instability of the L1$_0$ ordered phase in FePd nanoparticles 3-14 nm in diameter.

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