Effects of surface step and substrate temperature on nanostructure of L10-FePt nanoparticles

著者	Sato Kazuhisa, Kajiwara Takenori, Fujiyoshi Masaru, Ishimaru Manabu, Hirotsu Yoshihiko, Shinohara Tadashi
journal or publication title	Journal of Applied Physics
volume	93
number	10
page range	7414-7416
year	2003
URL	http://hdl.handle.net/10097/52169

doi: 10.1063/1.1541641

JOURNAL OF APPLIED PHYSICS VOLUME 93, NUMBER 10 15 MAY 2003

Effects of surface step and substrate temperature on nanostructure of $L1_0-$FePt nanoparticles

Kazuhisa Sato,[a] Takenori Kajiwara, Masaru Fujiyoshi, Manabu Ishimaru, and Yoshihiko Hirotsu
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Tadashi Shinohara
Hitachi Metals, Limited, 2-1, Shibaura 1-chome, Minato-ku, Tokyo 105-8614, Japan

(Presented on 13 November 2002)

The variation of the particle size, particle density, and its relation to the hard magnetic properties of FePt nanoparticles with respect to substrate temperatures and substrate surface morphologies has been investigated. On geometrically flat surfaces, densely dispersed FePt nanoparticles with a particle density of 10^{12} cm^{-2} were obtained at a substrate temperature below 573 K, while substrate temperatures between 623 and 823 K are necessary for obtaining well-oriented and well-isolated $L1_0-$FePt nanoparticles with large coercivity. Isolated particles fabricated above 573 K did not coalesce largely upon annealing at 873 K, which can be attributed to the ‘‘anchoring effect’’ of Pt ‘‘seed’’ particles. The coercivity of FePt nanoparticles was measured at 300 K damped with decreasing particle sizes below 10 nm. High-density areal packing of Fe/Pt nanoparticles could be fabricated at 673 K on a slightly inclined NaCl(001) substrate with surface steps. These particles coalesced easily upon annealing along the ⟨100⟩ step edges. [DOI: 10.1063/1.1541641]

I. INTRODUCTION

Recent developments of high-density magnetic recording media require a higher storage density with very fine magnetic grains of media materials as small as 10 nm in size. Nanometer-sized isolated magnetic particles of $L1_0$-type ordered alloys with high magnetoanisotropy are now attracting much interest because of their high thermal stability against superparamagnetic behavior. The $L1_0$-type FePt ordered alloy is known as a hard magnet with a high magnetocrystalline anisotropy as high as 7×10^6 J m^{-3} (Ref. 1). Though there are a lot of reports on nanostructure and hard magnetic properties of FePt nanoparticles in recent years, there are few articles concerning the particle size distribution and its relation to the hard magnetic properties.[2] For example, the size dependence of coercivity, especially for FePt nanoparticles with sizes smaller than 10 nm has not been made clear yet in spite of interests both from scientific and industrial aspects. A systematic understanding of hard magnetic properties in relation to the particle morphology and atomic long-range order (LRO) is necessary for the $L1_0-$FePt nanoparticles. The development of techniques for the enhancement of particle density without a particle coalescence is also important for future applications. A technique with a successive Fe deposition on Pt ‘‘seed’’ particles followed by annealing for the $L1_0-$FePt nanoparticles formation[3] has been developed, which is thought to be one of the techniques to overcome the particle coalescence during annealing due to the ‘‘anchoring by the seeds.’’ Also, metal deposition onto substrate steps can be considered for one of the candidates for fabricating nanoparticles with higher density, since particles tend to trap along the step edges.[4] In this study, using the successive Fe/Pt deposition technique, we have investigated the variation of the particle size, particle density of FePt nanoparticles, and their hard magnetic properties with different substrate temperatures and substrate surface geometrical conditions.

II. EXPERIMENT

FePt nanoparticles were fabricated by an electron-beam evaporation technique using pure Pt, Fe, and Al_2O_3 crystals as evaporation sources. NaCl(001) single crystals cleaved in air were supplied as substrates (5×5 mm^2 in size). After the cleavage, NaCl crystals were supplied into a vacuum chamber and heated at temperatures between 313 and 823 K in order to degas the substrate surfaces prior to the metal deposition. Besides the (001) cleaved crystals, NaCl crystals cleaved with an off angle (about 2–3°) were also prepared for the formation of surface steps. The off-angle NaCl substrates were heated at 673 K during the deposition. The deposition process took advantage of the overgrowth of Fe particles onto the Pt seed particles, which were grown initially on the NaCl substrates. The deposited thicknesses, monitored by a quartz oscillator both for Pt and Fe, were about 1 nm. Amorphous Al_2O_3 film was further deposited to protect the Fe particles from oxidation. Postannealing of as-deposited nanocomplex particles of Fe and Pt (hereafter, Fe/Pt) lead to a formation of $L1_0$-type FePt ordered nanoparticles. Annealing was performed at 873 K for 1 h with heating and cooling rates of about 5 and 10 K/min, respectively. Details of deposition method are described

---

[a] Electronic mail: sato@sanken.osaka-u.ac.jp

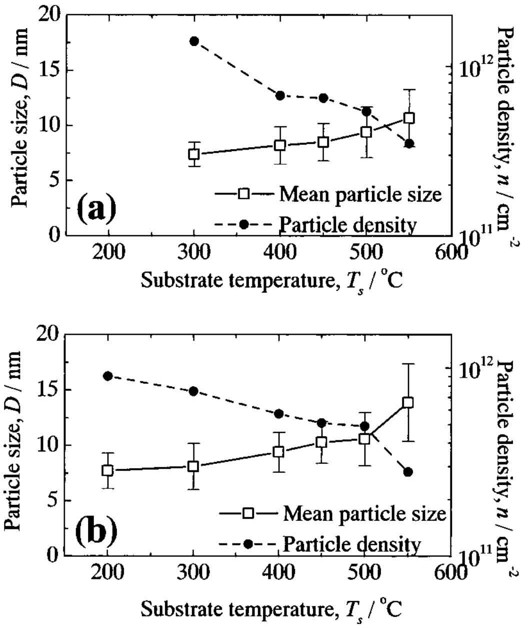

FIG. 1. Substrate temperature dependence of mean particle size (D) and particle density (n) for as-deposited (a) and annealed (b) specimens. Annealing condition was 873 K for 1 h. Particle size did not increase so largely by annealing, indicate the existence of anchoring effect of Pt seed particles.

elsewhere.[3,4] Specimen characterization was performed by transmission electron microscopy (TEM) and electron diffraction operated at 200 and 300 kV. The magnetic properties were measured by a superconducting quantum interference device (SQUID) magnetometer. Energy dispersive x-ray spectroscopy revealed that all specimens have mean Pt compositions between 43 and 54 at. % Pt.

III. RESULTS AND DISCUSSION

A. Variation of nanostructure and coercivity with substrate temperature

Particle isolation, size, and density on the flat NaCl substrate surface cleaved along (001) depend on the substrate temperature. Figure 1 shows the substrate temperature dependence of mean particle size and particle density for as-deposited [Fig. 1(a)] and annealed (873 K-1 h) [Fig. 1(b)] specimens. It was found that in obtaining a well-oriented Fe/Pt nanoparticles, substrate temperatures higher than 623 K are necessary for an as-deposited specimen. The isolation of particles was achieved with substrate temperatures higher than 573 K. For well-oriented and well-isolated nanoparticles, their particle densities were in the range of 10^{11} cm^{-2}. Mean particle sizes become slightly larger with increasing substrate temperatures, but the sizes did not change largely upon annealing at 873 K as shown in Fig. 1(b).

Large coercivities were obtained for specimens fabricated under the substrate temperatures higher than 623 K as shown in Fig. 2. All the specimens were heat treated at 873 K for 1 h. Besides the atomic ordering by annealing, the reason for the increase of coercivity with substrate temperature can be attributed to the increase of particle size and the proceeding of particle isolation, which are expressed by the gradual decrease of density as shown in Fig. 1(b).

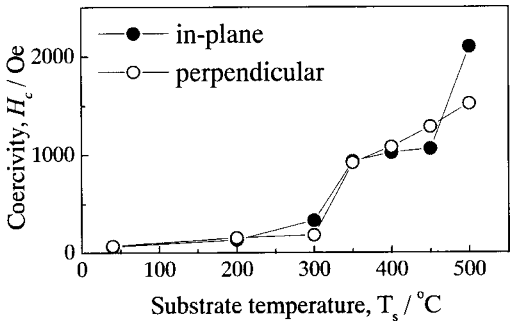

FIG. 2. Substrate temperature dependence of coercivity measured at 300 K both for perpendicular and in-plane direction. All the specimens were annealed at 873 K for 1 h. Coercivities largely enhanced for specimens fabricated at the substrate temperatures above 623 K.

About the relation between size and coercivity, we obtained a result showing an obvious decrease of coercivity with decreasing particle size as shown in Fig. 3. Luo and Sellmyer[5] have also reported the decrease of coercivity with sizes for their FePt:$\mathrm{SiO_2}$ granular thin films. Solid and open circles in Fig. 3 indicate the coercivities measured at 300 and 10 K, respectively. Specimens were annealed at 873 K for 1 h. The decrease of coercivity measured at 300 K with size can be explained by the increase of thermal fluctuation of the magnetic moments. On the other hand, the decrease of coercivities with the particle sizes at 10 K, though their values are larger than that of 300 K, can be attributed to the decrease of the LRO parameter with particle size. We obtained the LRO parameter of about 0.3–0.4 for 8 nm-sized FePt nanoparticles (coercivity was 340 Oe at 300 K; see Fig. 3), while the LRO parameter for 12 nm-sized FePt particles was about 0.6 with coercivity of 5.5 kOe at 300 K (Ref. 6). As another reason for the decrease of coercivity with particle size, the following reason can be considered: For specimens fabricated below 573 K, there are very fine particles with high packing density [Fig. 1(b)], which results in a magnetic coupling among the particles nearly contacted with each other causing the decrease of coercivity.[7] So, finally, it is concluded that for obtaining well-oriented and well-isolated $\mathrm{L1_0}$–FePt nanoparticles with a large coercivity, substrate temperatures between 623 and 823 K are necessary for our fabrication method using the Pt seed particles.

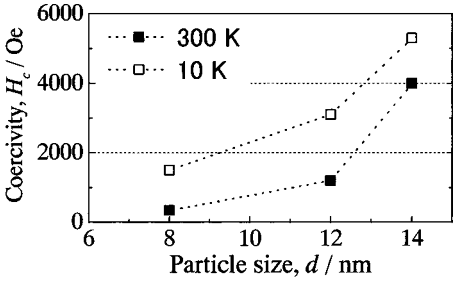

FIG. 3. Particle size dependence of coercivity for FePt nanoparticles after annealing at 873 K for 1 h. Measurements were done with applied magnetic field parallel to the film plane. Coercivity was greatly damped with decreasing the mean particle size both for 300 and 10 K.

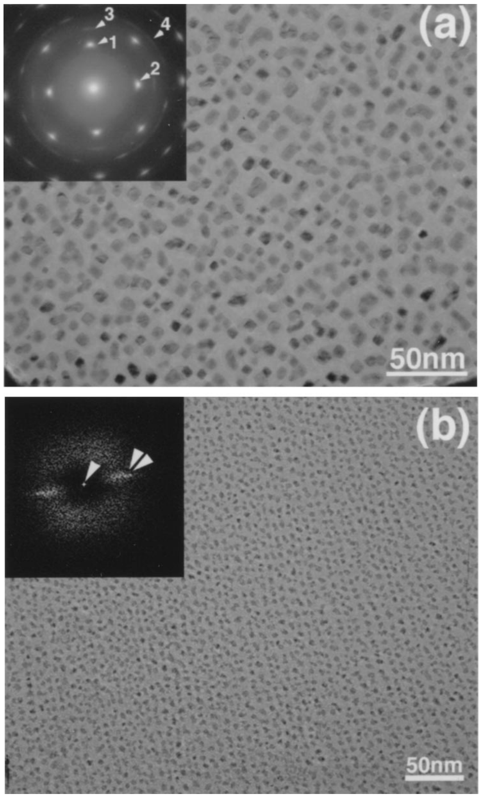

FIG. 4. TEM images of Fe/Pt nanocomplex particles deposited at 673 K on exact (001)- (a) and misoriented (001)-NaCl substrates (b). Indices of reflections marked by arrow in the SAED pattern [Fig. 1(a)] are as follows: (1) 200 Pt, (2) 020 Pt, (3) 200 Fe, and (4) 211 Fe. Single and double arrows in Fig. 1(b) denote the center of Fourier transformed pattern and the first-order satellite reflections, respectively.

B. FePt nanoparticles on off-angle NaCl substrate

Figures 4(a) and 4(b) show TEM images of Fe/Pt nanocomplex particles deposited on exact (001)- and slightly misoriented (001)-NaCl substrates with a common substrate temperature of 673 K, respectively. Selected area electron diffraction (SAED) patterns were almost the same. The SAED pattern in Fig. 1(a) reveals the epitaxial relationship between face-centered-cubic (fcc) Pt and body-centered-cubic (bcc) Fe as follows:[4] Fe[100]//Pt[100], Fe(011)//Pt(010). In Fig. 1(a), 9 nm-sized particles (9 ± 2 nm) are observed with a particle density of 6.7×10^{11} cm^{-2}. Among these particles, the particle coalescence seldom occurred upon annealing at a higher temperature as high as 873 K, which can be attributed to the ‘‘anchoring effect’’ of Pt seed particles on the coalescence. On the other hand, by using the misoriented NaCl as a substrate, 4 nm-sized particles (4 ± 1 nm) are formed along the $\langle100\rangle$ step edges with an average particle edge-to-edge distance of about 10 nm in Fig. 4(b). The particle density is 1.5×10^{12} cm^{-2}, which is two times larger than that of Fe/Pt nanoparticles grown on the flat NaCl(001) surface at 673 K [Fig. 1(a)]. Fourier transform of the image attached in the inset [Fig. 4(b)] clearly shows the first-order satellite reflections (marked by a double arrow) due to the periodically distributed Fe/Pt nanoparticles, which indicated the existence of widely spread periodic surface steps with a period of about 20 nm. We confirmed that these well-aligned regions are distributed in a wide area as wide as 1×10^4 μm^2 on the substrate by bright-field TEM observation. Our present study suggests that periodically arranged surface steps on a misoriented substrate are useful to obtain small-sized (smaller than 5 nm) Fe/Pt nanoparticles with a homogeneous size and a high particle density. Though, post-annealing at temperatures above 773 K induced a large coalescence of 4 nm-sized particles grown on the surface steps. Particles are easily contacted with each other along the $\langle100\rangle$ step edges above 773 K. So, it was difficult to obtain 4 nm-sized L1_0–FePt nanoparticles with a large coercivity since it was hard to promote the atomic ordering reaction without particle coalescence.

IV. CONCLUSION

Densely dispersed FePt nanoparticles with particle density of 10^{12} cm^{-2} were obtained at substrate temperatures below 573 K, while substrate temperatures between 623 and 823 K are necessary for obtaining well-oriented and well-isolated L1_0–FePt nanoparticles with a large coercivity. The isolated particles fabricated above 573 K did not coalesce largely upon annealing at 873 K, which can be attributed to the anchoring effect of Pt seed particles. The coercivity of FePt nanoparticles, measured at 300 K, damped with decreasing particle sizes below 10 nm. High-density areal packing of Fe/Pt nanoparticles, 4 nm in diameter, and 1.5×10^{12} cm^{-2} in density, was fabricated at 673 K by using a slightly inclined NaCl(001) surface as a substrate, while it turned out to coalesce easily upon annealing along the $\langle100\rangle$ step edges.

ACKNOWLEDGMENTS

The authors wish to thank Professor T. Kawai and Dr. H. Tanaka of ISIR, Osaka University for supporting the SQUID measurement. This study was supported by the Center of Excellence (COE) program at ISIR, Osaka University, Grant-in-Aid for Scientific Research (Nos. 13555189 and 14205094), and Special Coordination Funds for Promoting Science and Technology on ‘‘Nanohetero metallic materials’’ from the Japanese Ministry of Education, Culture, Sports, Science, and Technology.

[1] O. A. Ivanov, L. V. Solina, V. A. Demshila, and L. M. Magat, Phys. Met. Metallogr. **35**, 92 (1973).
[2] S. Sun, C. B. Murray, D. Weller, K. Folks, and A. Moser, Science **287**, 1989 (2000).
[3] B. Bian, K. Sato, Y. Hirotsu, and A. Makino, Appl. Phys. Lett. **75**, 3686 (1999).
[4] B. Bian, Y. Hirotsu, K. Sato, T. Ohkubo, and A. Makino, J. Electron Microsc. **48**, 753 (1999).
[5] C. P. Luo and D. J. Sellmyer, Appl. Phys. Lett. **75**, 3162 (1999).
[6] K. Sato, B. Bian, and Y. Hirotsu, J. Appl. Phys. **91**, 8516 (2002).
[7] B. Bian, K. Sato, T. Ohkubo, Y. Hirotsu, and A. Makino, J. Magn. Soc. Jpn. **23**, 736 (1999).