Effect of Growth Temperature on the Shape and Crystallinity of Chemically Produced FePt Nanoparticles

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The process of preparation of FePt nanoparticles was investigated with emphasis on the effect of "growth temperature," at which the atomic diffusion between Pt-rich and Fe-rich phases leads to the formation of uniform nanoparticles. Consequently, it was demonstrated that by controlling the growth temperature, the shape and crystallinity of FePt nanoparticles can be controlled. On the other hand, the size and composition were almost invariable at 5.6 ± 0.5 nm and $Fe_{53}Pt_{47}$, respectively.

FePt alloy particles with the $L1_0$ structure possess a very high uniaxial magnetic anisotropy. Superparamagnetic fluctuation of room-temperature magnetization can thus be suppressed even for particles of 2.7–3.0 nm in diameter, making an appropriate array of these nanoparticles a promising candidate for future ultra-high density magnetic recording media of $>1\,\mathrm{Tbit{\cdot}in^{-2}}$.

Since the preparation of FePt nanoparticles by Sun et al.,[1] many researchers have paid an attention on such nanoparticles.[2–5] We focused our effort on formation[1] of $L1_0$–FePt nanoparticles, because they can be fixed and aligned on the substrate more easily than FePt nanoparticles. In this study, we aimed at chemically producing $L1_0$–FePt nanoparticles with a controlled shape and grain size. To control the size, shape, and composition, we focused our attention on the crystal growth temperatue as the temperature at which the atomic diffusion between Pt-rich and Fe-rich phases leads to the formation of uniform nanoparticles for the $L1_0$–FePt nanoparticles and evaluated the effect of the growth temperature on magnetic properties obtained after annealing.

FePt nanoparticles were chemically produced by mixing oleic acid and $Fe(CO)_5$ with a benzyl ether/1-octadecene solution of $Pt(acac)_2$ and heating the mixture to the "mixing temperature" of 120 °C for about 5 min before oleylamine was added. Pt-rich nuclei were formed from the reduction of $Pt(acac)_2$ that took place simultaneously with a partial decomposition of $Fe(CO)_5$ at temperatures lower than 185 °C. This process allowed the existing Pt-rich nuclei to be coated with additional Fe atoms, thus forming larger clusters at a higher temperature. Heating the clusters by refluxing at the growth temperature led to the atomic diffusion and the formation of fcc-structured FePt nanoparticles. In the case of the presence of an excess $Fe(CO)_5$, the extra Fe atoms continue to coat the fcc nanoparticles, leading to the core/shell structure of FePt/Fe, and the top layer is oxidized to form $FePt/Fe_3O_4$. The mixture was heated at a growth temperature between 195 and 275 °C for up to 2 h. A black product was precipitated by adding ethanol to the mixture, which was then cooled to room temperature, separated by centrifugation and redispersed in hexane. Post-synthesis annealing of the nanoparticles was carried out at 600 °C for 3 h under the flow of N_2 gas.

The shape and crystallinity of chemically produced FePt nanoparticles depended on the growth temperature, whereas no such temperature dependence was observed for their size and composition. The FePt nanoparticles obtained at a growth temperature lower than 215 °C and higher than 255 °C have a spherical shape with an estimated average size of 5.6 ± 0.5 nm, while those obtained at the growth temperature between 215 and 255 °C have a cubic shape with an estimated average size of 5.5 ± 0.5 nm. Beside on Sun's group previous reports,[1] it was suggested that the treatment at the growth temperature of 215–255 °C is suitable for the preparation of cubic nanoparticles. On the other hand, the composition of chemically produced FePt nanoparticles is almost constant at $Fe_{53}Pt_{47}$ irrespective of the growth temperature.

Figure 1a shows a uniform arrangement of the chemically produced FePt nanoparticles at the growth temperature of 225 °C. The SAED ring image in Figure 1b identifies the crystal structure of the nanoparticles to be of formatted fcc phase. Similarly, the assembly in Figure 1c shows a uniform arrangement of the FePt nanoparticles prepared chemically at the growth temperature of 245 °C. Figure 1d shows a small portion of the area shown in Figure 1c at a higher magnetification. The shape of the chemically produced nanoparticles at the growth temperature of 245 °C suggested cubic, and the lattice constants of the nanoparticles were found to be $d(200) \cong 0.19$ nm and $d(111) \cong 0.23$ nm. It is suggested that the crystallinity of the nanoparticles is essentially that of the fcc phase. However, the assembly shown in Figure 1e exhibits four bright reflections (all in the (200) ring) linked by a fourfold symmetry, making the diffraction intensity strong for the (200) ring. Figure 1e also shows that the (111) ring has no bright reflections, making its diffraction intensity very weak. These results indicate that the arrangement of FePt nanoparticles in Figure 1c is (100) textured. Based on Sun's group previous reports,[1] it is expected the (100) textured nanoparticles exhibits cubical shape. Additionally, it was confirmed that the fourfold symmetry resulted from fct–FePt(001). Although the fct phase contained in the nanoparticles is a small amount by can the characterization not in XRD profile[6] only by TEM image of the nanoparticles, showing that the crystallinity of the nanocubes at the growth temperature of 245 °C is not only fcc phase but also partial fct phase structure. Thus, we succeeded in controlling the shape and crystallinity of partial $L1_0$–$Fe_{52}Pt_{48}$ cubic nanoparticles with monodispersion.

Coercivity and magnetic squareness of the hysteresis loop of the FePt nanoparticles after post-synthesis annealing at the tem-

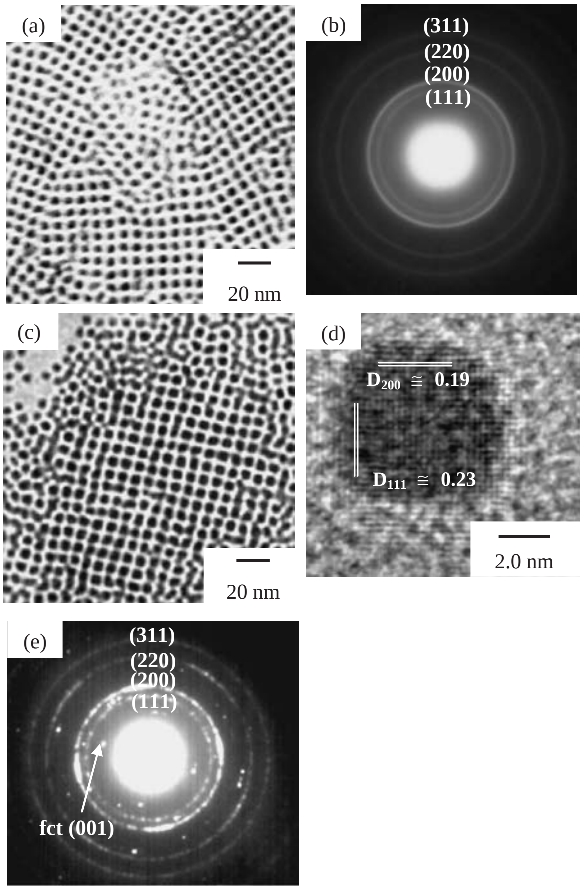

Figure 1. Chemically produced FePt nanoparticles at the growth temperature of 225 and 245 °C. (a) TEM image, (b) selected area electron diffraction (SAED) image patterns at 225 °C, where (111), (200), (220), and (311) indicate the four rings of the nanoparticle structure. (c), (d) are TEM images and (e) is SAED image patterns at 245 °C, where (111), (200), (220), and (311) indicate the four major orientations, and fct(001) indicates the four spots of the nanoparticle structure.

perature of 600 °C for 3 h under the flow of N_2 gas atmosphere as functional growth temperature are shown in Figure 2. It can be seen that the coercivity and magnetic squareness of the nanoparticles after annealing increased with growth temperature up to ca. 245 °C, and then they decreased at higher temperature. It was confirmed that the crystallinity of annealed nanoparticles was improved from fcc to fct phase. But the $L1_0$ ordering was not complete because of remaining fcc phase and increasing reflection peaks of Fe oxide. Therefore, magnetization of annealed nanoparticles changed despite the constant annealing condition such as a temperature. However, it was suggested that the crystallinity of produced FePt nanoparticles before annealing procedure affects the magnetization of FePt nanoparticles throughout the post-annealing process. Especially, the growth temperature of 245 °C is in most suitable for $L1_0$ ordering. Although the $L1_0$ ordering of FePt nanoparticles was improved by annealing procedure, it was confirmed the magnetization of the annealed FePt nanoparticles is lower than expected. There is a possibility that the annealed FePt nanoparticles were not single crystalline and contained nonmagnetic materials such as Fe oxide or carbon.

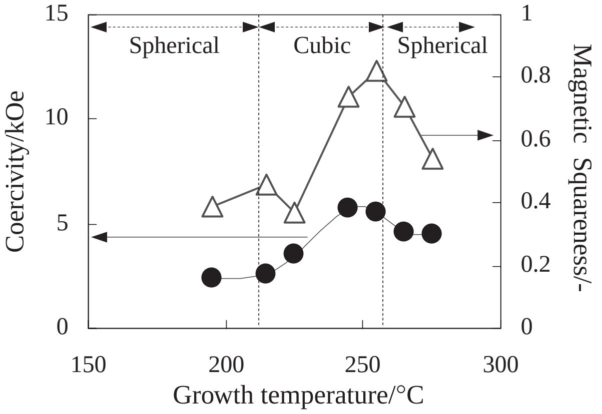

Figure 2. Influence of growth temperature on magnetic properties of FePt nanoparticles after annealing at 600 °C for 3 h under the flow of N_2 gas as functional of growth temperature. ●: Coercivity, △: Magnetic squareness.

Consequently, the results presented in this paper demonstrate that we succeeded in producing FePt nanoparticles with a controlled shape and a uniform size distribution, and that the crystallinity of FePt nanoparticles improved as the growth temperature was increased. It is suggested that the magnetic properties of annealed, chemically produced FePt nanoparticles are dependent on the shape and crystallinity before annealing. This study thus demonstrates that by controlling the growth temperature, the shape and crystallinity of FePt nanoparticles can be controlled.

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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