Rapid thermal annealing of FePt nanoparticles

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We report a systematic study on rapid thermal annealing (RTA) of FePt nanoparticles. FePt particles with an average size of 8 nm were synthesized by a chemical solution method, and then annealed using RTA and conventional furnace annealing (FA). It was observed that FePt nanoparticles can be transformed from disordered A1 phase to ordered L10 phase at 650 °C for 10 s using RTA, which is much shorter than the time needed for FA. The transmission electron microscopy and x-ray diffraction studies have revealed that the particle agglomeration and grain growth in the RTA treated samples are much less than in the FA treated samples. A linear correlation between the coercivity and the square root of the treatment time was observed in the RTA treated samples, which implies that the phase transition is related to atomic diffusion of Fe atoms from Fe-rich shells into the Pt-rich cores. © 2008 American Institute of Physics. [DOI: 10.1063/1.2953078]

I. INTRODUCTION

FePt nanoparticles have drawn great attention in the past years due to the potential applications in many areas including data storage, permanent magnets, and biomedical technology.1–7 High uniaxial magnetocrystalline anisotropy of the L10 FePt phase is one of the key properties for those applications.8 Unfortunately, as-synthesized FePt particles take a disordered A1 structure which has vanishingly small magnetocrystalline anisotropy. Therefore postsynthesis annealing is necessary to transform the disordered A1 phase to the ordered L10 phase. However, the heat treatment always causes sintering and agglomeration of FePt nanoparticles and leads to destruction of monodispersion of the nanoparticles. This undesired morphology change is a severe problem for many applications which require a morphology control in the nanostructured materials. Many studies have been done to solve the problem and to produce monodisperse FePt nanoparticles. For example, the salt-matrix annealing is an effective method to produce monodisperse L10 structured FePt nanoparticles by using salts as the separating media.9–13 Coating of high-melting-point materials on FePt particles can also be a good technique to prevent agglomeration and sintering.14,15 Controlling annealing time is another option to reduce the sintering by limiting interdiffusion between nanoparticles. Recently, the rapid thermal annealing (RTA) technique has been applied for magnetic materials with which samples can be heated to high temperature in a time scale of seconds.16–18 Zeng et al.19 reported that the chemical ordering of 4 nm FePt particles starts at the temperature of 400 °C by using RTA, which is lower compared to conventional furnace annealing (FA) and a short annealing time results in reduced sintering of particles. However, there has not been an in-depth study reported of the correlation between magnetic hardening and morphology change in RTA treated FePt nanoparticles. In this paper, we report a systematic study on effects of annealing temperature and time on the L10 phase formation and morphology change of FePt nanoparticles induced by RTA.

II. EXPERIMENTS

8 nm FePt nanoparticles were prepared via chemical solution route consisting of reduction in Pt(acac)2 and decomposition of Fe(CO)5 under argon gas flow. To obtain 8 nm particles instead of 4 nm ones, the synthesis procedure is slightly different from the method used in Ref. 1 In a typical procedure, 0.5 mmol of Pt(acac)2 and 10 ml of octyl ether were added in a 125 ml flask with a magnetic stir bar. After purging argon gas for 20 min, the flask was heated up to 110 °C for 10 min. After the Pt precursor dissolved completely at 110 °C, 0.4 mmol of oleic acid and 0.4 mmol oleyl amine were added into the flask followed by 0.75 mmol of Fe(CO)5. The flask was then heated up to 300 °C and refluxed for 1 h. After Fe(CO)5 was added, the solution color changed from transparent yellow to black which suggests the formation of FePt nanoparticles. After the reflux, the flask was cooled down to room temperature under argon flow. It should be noted that cubic particles were formed instead of spherical particles, as reported in Ref. 1, due to the difference in the synthesis procedure (e.g., 1,2-hexadecanediol was not used). The cubic shape may also be explained by the molecular structure of the solvent.20 The black particles were precipitated after adding 35 ml of ethanol and separated by centrifugation at 6000 rpm for 20 min. The precipitated particles were then dispersed in 10 ml of hexane. In order to remove the extra surfactant completely, the centrifugation was repeated twice. Final products were dispersed in 10 ml hexane.

The dispersed FePt particles were deposited on a Si substrate and annealed at different conditions using the RTA facility (Modular Process Technology model RTP-600S rapid thermal processing system) and a FA facility under forming gas (93% Ar+7% H2) flow after evaporating hexane at room temperature. The magnetic measurements were carried out using alternating gradient magnetometer and superconduct-
ing quantum interference device magnetometer with a magnetic field up to 7 T. The transmission electron microscopy (TEM) was used for morphology observations. The composition of the particles (around Fe₅₀Pt₅₀) was checked by energy dispersive x-ray spectroscopy. X-ray diffraction (XRD) was used to determine the phase transition of FePt nanoparticles with a CuK_α radiation (λ = 1.5405 Å).

### III. RESULTS AND DISCUSSIONS

Heat treatments of the as-synthesized FePt nanoparticles lead to formation of the L₁₀ phase. It is important to know how short the phase transition from A₁ to L₁₀ is needed. Advantages of RTA include fast heating/cooling and controllable short annealing time, compared with conventional FA. Figure 1 shows the XRD patterns of the as-synthesized and the as-annealed FePt particles by using RTA and FA. In Fig. 1(a), the strongest (111) peak at 40.5° corresponds to the face-centered cubic structure obtained from the randomly oriented particles. The grain size calculated by Scherrer’s equation is around 8 nm. As shown in Fig. 1(b), the (111) peak of the RTA treated FePt nanoparticles shifted to 41° and the superlattice (001) and (110) peaks showed up after the annealing, indicating the formation of the L₁₀ ordered phase within 5 s at 650 °C. The particle size of 650 °C×5 s RTA treated particles is calculated as 12 nm compared to 27 nm for 650 °C×10 min FA treated particles [Figure 1(c)]. It should be noted that the XRD analysis gives only grain size instead of particle size.

Figure 2 shows the grain size dependence on annealing time for RTA and FA at 650 °C. The grain size increases with annealing time for both annealing methods. However, the “saturation” grain size of 17 nm for RTA is much smaller than that of the size of 30 nm for FA, indicating that RTA leads to much less particle sintering and grain growth. As we will see later, the grain growth saturation is accompanied by the magnetic hardening saturation.

Morphology observations have directly shown how the heat treatments affect the particle sintering and grain growth.
where $I_{001}$ and $I_{002}$ are the integrated intensities of the (001) and (002) diffraction peaks from the XRD patterns, respectively. To monitor the formation of $L_{10}$ phase induced by the heat treatments, FePt nanoparticles were annealed at 650 °C for different times by RTA. Figure 4 compares the dependence of $S$ and coercivity on annealing time for RTA treated samples. It was found that high $S$ value about 0.97 was achieved by RTA at 650 °C for only 10 s. The further RTA treatment, however, does not change $S$ anymore, indicating that the transformation from A1 to $L_{10}$ phase of the FePt nanoparticles was completed within 10 s at 650 °C. Since the magnetic hardening of the FePt nanoparticles is closely related to the chemical ordering parameter, the effect of annealing time on coercivity is similar to that on the chemical ordering parameter, although coercivity is not solely determined by crystalline parameters (it is also related to morphology of the particles). The RTA induced magnetic hardening within several seconds for other magnetic materials was also observed and discussed in other reports.23–25 This phenomenon may be explained by a lowered phase transition temperature in RTA treated samples. Figure 5 shows the demagnetization curve of the 8 nm FePt particles annealed at 650 °C for 10 s by RTA as an example. It was found that the squareness of the demagnetization curve is also very good even though the sample was heated for only 10 s. The energy product of the particles is around 12.7 MG Oe.

Since the magnetic hardening process of FePt particles is related to the atomic rearrangement from disordered A1 phase to ordered $L_{10}$ phase, it is reasonable to correlate an atomic diffusion process to the annealing process. In order to understand the magnetic hardening rate at various annealing temperatures, RTA was conducted at different temperatures for different time for the 8 nm FePt particles. Figure 6(a) shows the coercivity dependence on annealing time at different temperatures. It was found that the coercivity increases with increasing annealing time and temperature. The $H_c$ reaches its saturated value of 10 kOe within 60 s if the temperature is above 600 °C. However, for 500 °C annealing, the $H_c$ does not saturate even after 300 s and this particular sample has the ordering parameter of only 0.58, which suggests that the A1 to $L_{10}$ phase transformation cannot be completed at 500 °C for a short annealing time by RTA.

In addition, correlation between the coercivity and the square root of treatment time $\sqrt{t}$ of RTA treated samples was observed, as shown in Fig. 6(b). It is well known that the diffusion coefficient $D$ is expressed as

$$D = D_0 \exp \left( \frac{E}{kT} \right),$$

where $D_0$ is a constant (cm$^2$ s$^{-1}$), $E$ is the activation energy (eV), $T$ is the temperature (K) and $k$ is Boltzmann’s constant ($k=8.617 \times 10^{-5}$eV K$^{-1}$). Calorimetric studies of the A1 to $L_{10}$ transition in FePt particles have revealed that the activation energy of phase transformation is about 1.0–1.7 eV.26–28 A diffusion distance $x$ is given as...
has revealed that the average grain size of RTA treated samples is substantially smaller than that of the FA treated samples. A linear correlation between the coercivity and the square root of treatment time $\sqrt{t}$ was observed in the RTA treated samples.

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