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Sintering behavior of spin-coated FePt and FePtAu nanoparticles

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FePt and [FePt]_{0.95}Au_{0.05} nanoparticles with an average size of about 4 nm were chemically synthesized and spin coated onto silicon substrates. Samples were subsequently thermally annealed at temperatures ranging from 250 to 500 °C for 30 min. Three-dimensional structural characterization was carried out with small-angle neutron scattering (SANS) and small-angle x-ray diffraction (SAXRD) measurements. For both FePt and [FePt]_{0.95}Au_{0.05} particles before annealing, SANS measurements gave an in-plane coherence length parameter $a=7.3$ nm, while SAXRD measurements gave a perpendicular coherence length parameter $c=12.0$ nm. The ratio of c/a is about 1.64, indicating the as-made particle array has a hexagonal close-packed superstructure. For both FePt and FePtAu nanoparticles, the diffraction peaks shifted to higher angles and broadened with increasing annealing temperature. This effect corresponds to a shrinking of the nanoparticle array, followed by agglomeration and sintering of the nanoparticles, resulting in the eventual loss of positional order with increasing annealing temperature. The effect is more pronounced for FePtAu than for FePt. Dynamic coercivity measurements show that the FePtAu nanoparticles have both higher intrinsic coercivity and higher switching volume at the same annealing temperature. These results are consistent with previous studies that show that additive Au both lowers the chemical ordering temperature and promotes sintering. © 2006 American Institute of Physics.

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I. INTRODUCTION

Self-assembled FePt nanoparticles are considered to be attractive candidates for ultrahigh-density magnetic recording due to the high magnetocrystalline anisotropy and chemical stability.¹⁻⁶ It is normally found that the coercivity of the FePt nanoparticles increases when they are treated at high annealing temperature, which results from the high degree of chemical ordering and improved magnetocrystalline anisotropy. In addition, sintering of FePt nanoparticles occurs when they are annealed at high temperatures. The sintering process results in the loss of the positional order of the self-assembled particle array, which is undesirable for magnetic recording media, and there is no simple way to inhibit the agglomeration. Recent experiments show that some additives, such as Ag and Au, can lower the annealing temperature for phase transformation, as well as promote the particle aggregation.^{3,5,7}

Small-angle neutron scattering (SANS) is a powerful method to nondestructively characterize the structure of material with coherence length scales ranging from 1 to 100 nm. SANS measurements can be performed directly on thin film prepared on single-crystal wafers, which can be transparent to neutrons so that nearly the entire scattering

signal arises from the thin-film structure. Moreover SANS measurements can provide information about structures averaged over several square centimeters, providing a better statistically averaged measurement of the materials. In this article, the ordering and sintering behavior of spin-coated FePt and FePtAu nanoparticles were investigated by using SANS, small-angle x-ray diffraction (SAXRD), and magnetometry.

II. EXPERIMENT

The synthesis of FePt and [FePt]_{0.95}Au_{0.05} nanoparticles involved the thermal decomposition of Fe(CO)₅ and reduction of Pt(acac)₂ and gold acetate in an organic solvent, as described elsewhere.^{1,5} The average particle size of both FePt and [FePt]_{0.95}Au_{0.05} was about 4 nm. The nanoparticles were cast onto a Si wafer by spin coating. Samples were subsequently thermally annealed under flowing argon containing 5% hydrogen in a tube furnace with temperatures ranging from 250 to 500 °C for 30 min. The composition of FePt nanoparticles was determined by energy dispersive x-ray analysis on a Philips model XL 30 scanning electron microscope.

The SANS measurements were performed at ambient conditions on the 30 m NG3 SANS instrument at the National Institute of Standards and Technology (NIST) Center

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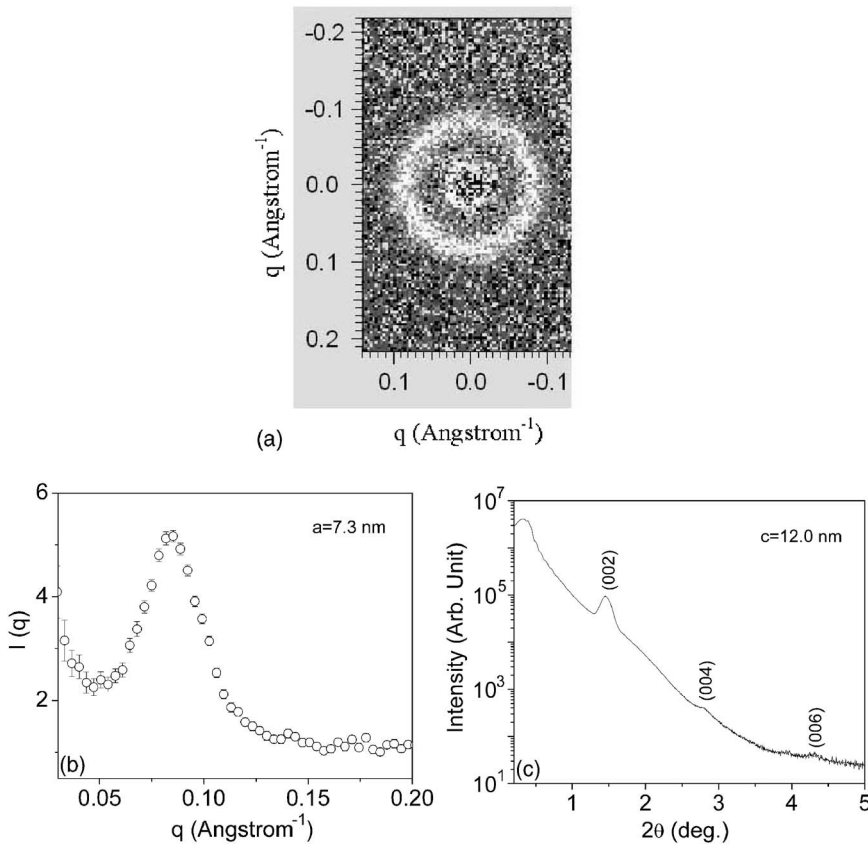


FIG. 1. (a) 2D SANS scattering pattern of as-made FePt nanoparticle. (b) Intensity I averaged on rings in (a) at constant scattering vector q as a function of q . (c) SAXRD pattern of as-made FePt nanoparticles.

for Neutron Research. Scattering data were collected on a two-dimensional (2D) detector and the scattered intensity was corrected using standard reduction methods. The wavelength for the neutrons was 0.6 nm. The distance between sample and detector was 1.33 m.

SAXRD measurements were performed in the reflection geometry with a Philips X'Pert Materials Research Diffractometer (X'Pert-MRD). Magnetic hysteresis curves and dynamic coercivity were measured on a Princeton Micromag 2900 alternating gradient magnetometer using a 19 kOe saturating field.

III. RESULTS AND DISCUSSION

The sample was placed normal to the neutron beam, and the SANS image was obtained using a 2D detector. Figure 1(a) illustrates a typical SANS image of as-made FePt nanoparticles. The intensity $I(q)$ obtained for this sample after averaging on a ring at constant q (where $q = (4\pi/\lambda)\sin(\theta/2)$ and θ is the scattering angle) is given in Fig. 1(b). The scattering intensity exhibits a well-defined peak at $q \approx 0.085 \text{ \AA}^{-1}$, indicating an in-plane coherence length $a = 7.3 \text{ nm}$. Moreover, SAXRD reflectivity measurements in Fig. 1(c) give a perpendicular coherence length $c = 12.0 \text{ nm}$. The ratio of c/a is about 1.64, indicating the as-made FePt nanoparticle array has the hexagonal close-packed superstructure. The SANS and SAXRD measurements on as-made FePtAu nanoparticles show very similar results, suggesting both as-made FePt and FePtAu nanoparticle arrays have the same hcp structure.

High-temperature annealing processes cause the organic coatings of the nanoparticles to decompose. Consequently,

the nanoparticles begin to move together causing the array to shrink. Eventually the particles become aggregated and sinter. The degree of sintering depends on the additives, annealing temperature, and time.^{2,3,5} SANS can clearly show the

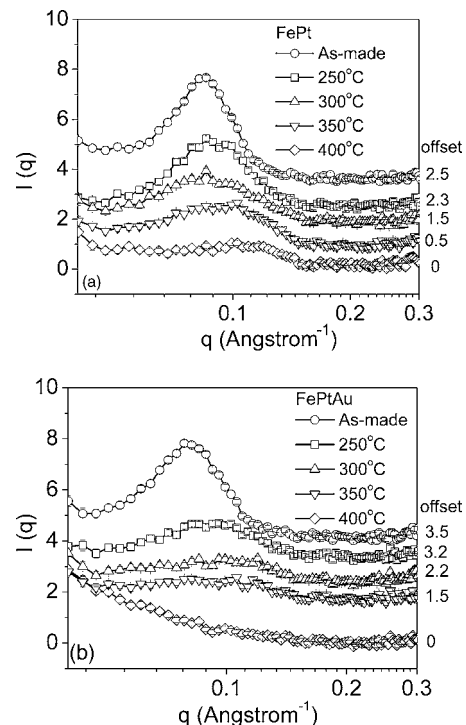


FIG. 2. Intensity I extracted from SANS images as a function of q for as-made and annealed (a) FePt and (b) FePtAu nanoparticles. The curves are vertically shifted, as shown by the offset.

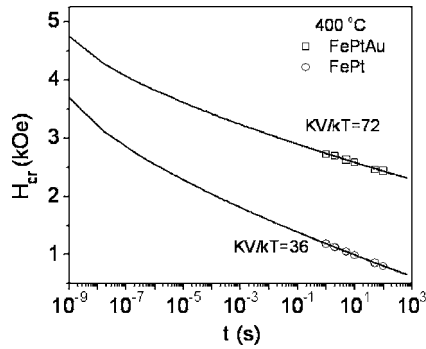


FIG. 3. Time dependence of coercivity for FePt and FePtAu nanoparticles annealed at 400 °C for 30 min. The lines are fits based on Sharrock's formula [Eq. (1)].

evolution of the degree of order of the FePt and FePtAu nanoparticle arrays as a function of annealing temperature. Figure 2(a) illustrates the scattering intensity $I(q)$ versus q extracted from the 2D SANS images for FePt nanoparticles annealed from 250 to 400 °C. There is no significant change for FePt nanoparticles with annealing temperature up to 300 °C. The peak is located at almost the same position with a small broadening. It is well known that the organic coating starts to decompose at a temperature around 350 °C.⁸ Further increase in the annealing temperature results in decomposition of the surfactants, and the SANS peak rapidly shifts to higher q value, indicating shrinking and sintering of the FePt nanoparticle array. The effect is more pronounced for FePtAu than for FePt. Figure 2(b) shows the scattering intensity $I(q)$ vs q for FePtAu nanoparticles annealed from 250 to 400 °C. The SANS peak for FePtAu nanoparticles shifts to higher q value at low annealing temperature (250 °C) and the peak completely disappears at high annealing temperature (350 °C). This suggests that Au additives contribute significantly to the sintering of the FePt nanoparticles. Since Au atoms have low surface energy that favors surface segregation,⁵ the FePtAu nanoparticles array have a tendency to lose their positional order at low annealing temperature, even below the temperature at which the surfactants decompose.

Figure 3 shows the time dependence of the remanence coercivity for the FePt and FePtAu nanoparticles annealed at 400 °C for 30 min. The smooth curve through the data is a fit using Sharrock's formula,⁹

$$H_{cr} = H_0 \left[1 - \left(\frac{k_B T}{K_u V} \ln(f_0 t) \right)^{2/3} \right], \quad (1)$$

where H_0 is the short-time coercivity, K_u the anisotropy energy density, V the particle volume, k_B Boltzmann's constant, T the absolute temperature, f_0 the attempt frequency ($\sim 10^9$ Hz), and t the wait time at reverse field. The 2/3 exponent is appropriate for randomly oriented easy axes. From the fit parameters, the intrinsic remanent coercivity H_0 and thermal stability factor $K_u V/kT$ can be determined. For FePtAu nanoparticles annealed at 400 °C, H_0 is about 4.7 kOe, which is more than 27% larger than that of the FePt nanoparticles (~ 3.7 kOe). Moreover, $K_u V/kT$ of FePtAu nanoparticles is twice as large as that of the FePt nanoparticles, indicating the FePtAu nanoparticles have large aggregates and switching volume after annealing. These results are consistent with previous studies that show that additive Au both lowers the chemical ordering temperature and promotes sintering.⁷

In summary, the spin-coated FePt and FePtAu nanoparticles have a hcp ordered superstructure. The annealing process, which is needed to achieve hard magnetic properties, destroys the assemblies via agglomeration and sintering based on SANS and magnetic measurements. This effect is more pronounced for FePtAu nanoparticles than for FePt nanoparticles.

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